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**Colour and Chloride Removal from Pulp Mill Effluent
Using Ion-Exchange**

by

Giyeon Yun



A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Master of Science

in

Environmental Engineering

Department of Civil and Environmental Engineering

Edmonton, Alberta

Fall, 2001

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled COLOUR AND CHLORIDE REMOVAL FROM PULP MILL EFFLUENT USING ION EXCHANGE submitted by GIYEON YUN in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in ENVIRONMENTAL ENGINEERING.

ABSTRACT

Pulp and paper mills face stringent effluent discharge regulations and have acknowledged that it is necessary to look into innovative technologies to recycle considerable amount of effluent rather than discharging into surface water. The pulp and paper industry has made efforts to reduce pollutants in effluents from mills and to approach zero effluent discharge.

Coloured effluents from mills give rise to aesthetic unpleasantness. To cope with more stringent effluent discharge regulations and to protect the ecosystem from harmful pollutants in the mill effluents, ion exchange was investigated on a bench scale to reduce colour and chloride in pulp mill effluents. Chloride is one of the non-process elements (NPE) in the mill systems, which are known to be harmful elements in pulping. Chloride was selected as surrogate measure of other NPEs.

The nine resins tested are weak basic anionic (WBA) resins including Amberlite® IRA67 and IRA92, and strong basic anionic (SBA) resins including Amberlite® IRA400, IRA402, IRA458, IRA900, IRA958, IRN78, and Amberjet® 4400OH. Batch testing has been conducted to select effective ion-exchange resins for colour and chloride removal and to determine effective regenerants for regeneration of exhausted resins.

The results from batch and column tests on decolourisation indicate that IRA958 has the potential to completely remove colour in the effluents. IRA458 and IRA900 also successfully removed colour. 1 *N* NaOH in combination with 1 *N* NaCl was found to regenerate the resins effectively to recover their original colour removal efficiency. The results of this study indicate that ion exchange technology may be applied to decolourise pulp mill effluents and aid in the drive toward progressive system closure.

IRN78 and 4400OH, which hold hydroxide ions as exchange groups, removed chloride in a modest removal efficiency up to 65%. Although this removal efficiency may not be sufficient, it implies a very important point that other NPEs, having higher affinity to the anionic resins than chloride, might be removed to greater degrees than was chloride. Regeneration of exhausted resins after chloride removal, using NaOH has been studied. However, it could not return the resins to their original chloride removal efficiencies.

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1 Introduction

The pulp and paper industry accounts for more contaminant discharge (on a mass basis) than any other industrial sector in North America (EPA, 1995). Discharge requirements are becoming increasingly stringent in an attempt to reduce the impact of these effluents on the environment. In response, the industry has instituted several process modifications to reduce the contaminant loading in their effluent streams. Of these contaminants, colour has proven to be particularly difficult to remove in a cost efficient manner. The colour in pulp mill effluent is caused by lignin and its derivatives that are separated from the wood fibres during the pulping process. Among other effects, this colour gives rise to aesthetic unpleasantness when it is discharged into the receiving water. If this water is used as a drinking water source, the colour causing compounds also result in an increased chlorine demand during the disinfection process of water treatment plants.

Pulp mills are also major users of fresh water. The industry has sought to reduce its fresh water requirements in recent years by increasing the amount of process water recycled internally. This effort is termed progressive plant closure, with the goal being to attain a zero liquid effluent status. The main obstacle to recycling large amounts of process waters in kraft pulp mills is the build-up of dissolved non-process elements (NPE) in the recycled water that adversely affect the pulp quality and process infrastructure.

Of these NPEs, chloride and potassium ions are the most difficult to remove from waste streams. Their build-up is known to cause clogging and corrosion in the chemical recovery system of pulp mills (Jemma *et al.*, 1997; Melanson, 2000). These problems would force a mill to shut down several times a year to remove the deposits and flush the systems.

The most widely used treatment method for pulp mill effluent entails biological treatment followed by solids separation by sedimentation. This approach is very efficient for the removal of readily biodegradable organics and suspended solids, but has little effect on dissolved NPEs and colour. Therefore, more advanced technologies are needed to deal with these contaminants. Among the diverse removal technologies proposed for this purpose, advanced treatment using ion exchange resins offers an attractive alternative to remove both colour and other NPE to facilitate progressive plant closure.

The potential benefits of applying ion exchange technology to treat pulp mill effluents include:

- Selective removal of cations and anions;
- Regeneration and re-use of exhausted resins;
- Facilitation of progressive system closure in the mills; and
- Prevention of the corrosion of chemical recovery system.

1.1 Objectives

The objective of this study is to assess the ability of selected ion exchange resins to remove colour and chloride from pulp mill effluents as a step toward progressive system closure. The scope of the investigation includes:

- Determination of effective resins for colour removal;
- Determination of effective resins for chloride removal;
- Determination of effective regenerant for exhausted resins after colour removal;
- Determination of effective regenerant for exhausted resins after chloride removal;
- Verification of the results from batch testing in column testing via breakthrough and elution studies; and
- Determination of the optimal point within the mill to apply the treatment technology.

2 Literature Review

2.1 Pulp Mill Processes

2.1.1 Pulp Mill Processes

Paper is composed of interlaced fibres. Although fibre can be obtained from practically any vegetative matter, the most abundant source of fibre is wood from trees. Therefore, the majority of the fibre used to make paper is derived from either hardwood or softwood trees. The fibres are glued together by lignin in their natural state, and the pulping processes are designed to separate the fibres from the lignin while causing the minimum amount of damage to the fibre. To this end, several different pulping processes have been developed ranging from methods which employ heat and mechanical energy to separate fibres to those which use of heat and chemicals to dissolve the lignin and free the fibre. This spectrum of methods includes: thermo-mechanical, chemi-mechanical, chemi-thermo-mechanical pulping, and chemical pulping. Mechanical pulping methods tend to damage the wood fibres somewhat, and so are suitable when low strength paper is desired. However, to produce a high strength pulp suitable for high quality paper, chemical pulping methods are required. Of these, the kraft process is the predominant process due to its ability to separate the fibres from the lignin while causing the least damage to the fibre. More than 73 million tonnes, or about 70% of the annual pulp production in the world is produced by the kraft pulping process (Alberta Pacific Forest Industries INC,

2000). In addition to producing a high strength pulp, the kraft process allows the recovery and reuse of the pulping chemicals, thereby reducing processing costs. In the kraft pulping process, wood chips are “cooked” at elevated temperature and pressure in the presence of caustic chemicals to dissolve the lignin. The kraft process forms the core of the overall pulp and paper making process shown in simplified form in Figure 2-1. The major stages in this process are:

- (1) Furnish preparation (including debarking and chipping);
- (2) Kraft pulping (including the recovery of pulping chemicals);
- (3) Bleaching; and
- (4) Product forming.

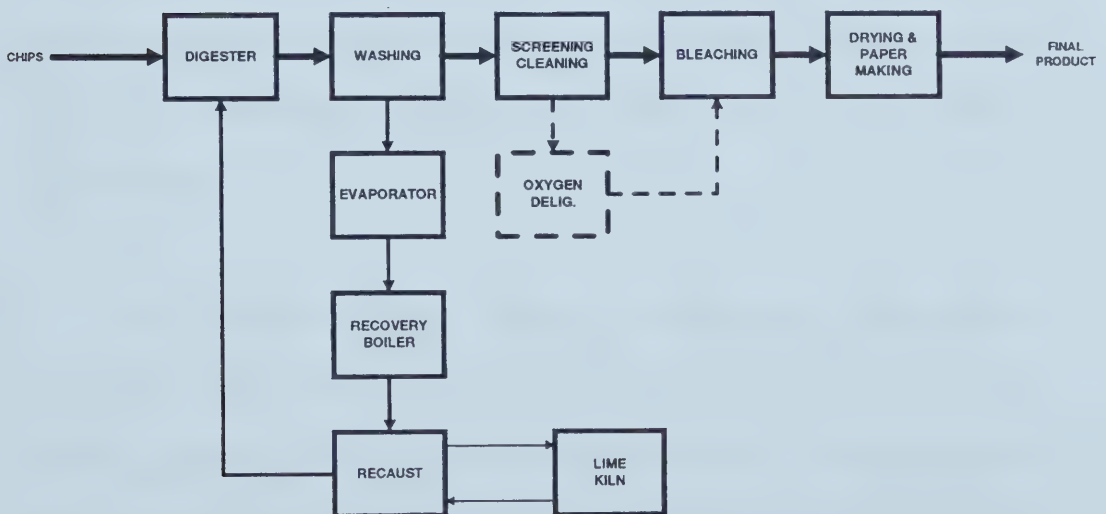


Figure 2-1 Kraft pulping process (after Alberta Pacific Forest Industries, Inc., 2000).

During the preparation of the furnish, wood logs are cut to size, the bark is removed and the debarked logs are then reduced to chips approximately 1 centimetre long. The chips are fed into a digester where the kraft process begins. In the digester, the wood chips are mixed with NaSO_2 (sodium sulfite) and NaOH (sodium hydroxide) and cooked under high pressure and temperature (Walden, 1985). The cooking temperature is 160 - 180°C as high as to cleave the ether bonds of lignin and remove other compounds (Solomon *et al.*, 1993). The mixture of these chemicals is termed the white, or cooking liquor. This step separates fibres from lignin. This results in a mixture of chips and cooking liquor called the brownstock. The brownstock then enters the washing and screening processes. At this point, the fibres are separated from the spent cooking liquors. The fibres continue to the next process step, which is generally to bleach the fibres to increase their brightness, and the spent liquors enter the chemical recovery loop within the kraft process. Up to this point, all the chemicals and water used for pulping are recycled within the mill via the chemical recovery system.

In the closed chemical recovery process, the used chemicals in the brownstock liquor are recovered. The brown liquor is concentrated by evaporation and then burned in a recovery boiler to consume the organic component and produce energy used to power the mill (other energy also is produced in the hog boiler which burns some or all of the bark). The inorganic chemicals form a molten smelt at the bottom of the furnace. The molten salt smelt containing mostly sodium sulfide and sodium carbonate is converted to green liquor when dissolved in water. This green liquor is

converted to white liquor when the sodium carbonate and calcium carbonate are converted into sodium hydroxide by lime addition in the recausticizing system. The white liquor is ready to be reused in the pulping process (Rapp & Pfromm, 1998). The lime is recovered in the recalcination kiln that converts calcium carbonate into lime by burning. The reconverted lime can then be reused in recausticizing system for slaking green liquor.

The separated unbleached fibres are still tinted brown because they still contain a number of organic components, mainly lignin, at low concentrations. The bleaching (purification) process that brightens the fibres is divided into two stages: an E_{op} (extraction reinforced with O_2 and H_2O_2) stage producing a caustic effluent and a D (bleaching reinforced with ClO_2) stage producing an acidic effluent. The bleaching process whitens and brightens the pulp and removes as much residual lignin as possible to create high quality pulp. After the bleaching process, the pulp looks like white cotton batten and is finally formed into sheets after dewatering. Some chemicals are added to increase strength and gloss.

2.1.2 Bleach Plant Sequences

The selection of chemicals used to bleach pulp has evolved over time from simple exposure to air and sunlight to the application of specific solutions of chemicals. For most of the last century, elemental chlorine was used as the predominant chemical in pulp bleaching because it produced a bright pulp at low cost without

significant damage to the fibre. However, in the late twentieth century, concern over chlorinated organics in the effluent, particularly dioxins and furans, prompted experimentation with alternative bleaching agents, particularly chlorine dioxide and hydrogen peroxide. Current *best practice* is to remove as much of the lignin as possible prior to the bleach plant by using extended digestion and oxygen delignification, and to replace elemental chlorine with chlorine dioxide or in the bleach plant sequence. This lowers the formation of adsorbable halogenated compounds (AO_X) to low levels, and this reduces the occurrence of dioxins and furans in the effluent to undetectable levels, as dictated by current regulatory standards. The evolution of the sequence of bleach plant chemicals over the last hundred years is summarized as:

- CEDED (until 1990) – Use of Elemental Chlorine
- DEDED (from 1990) – Elemental Chlorine Free (ECF)
- OQPE_{op}P (proposed, but rarely applied) – Total Chlorine Free (TCF)

where:

C = chlorine,

E_{op} = caustic extraction,

D = chlorine dioxide (ClO_2),

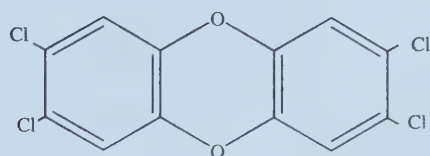
P = hydroxide (H_2O_2),

O = oxygen, and

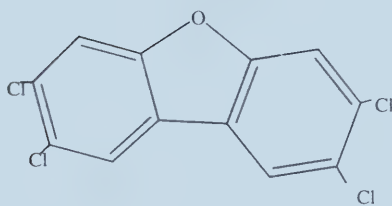
Q = chelant.

The use of elemental chlorine for the bleaching causes detectable levels of dioxins and furans in the receiving waters (especially 2,3,7,8-tetrachlorodibenzodioxin

(TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF), whose chemical structures given in Figure 2-2. The persistence, bioaccumulation, and potential toxicity of the polychlorinated dibenzo-p-dioxins and dibenzofuranes (PCDD/Fs) gave rise to great environmental concern (Berry *et al.*, 1991). The PCDD/Fs, which are extremely



TCDD



TCDF

Figure 2-2 Chemical structures of TCDD and TCDF (after Solomon *et al.*, 1993)

health-hazardous, have been restricted to extremely low levels in effluents by regulation (Folke, 1991). A summary of the Alberta kraft pulp mill discharge limits prepared by the Alberta Environment Department is given in Table 2-1.

This public health concern and the lowered production cost of chlorine dioxide led to the replacement of chlorine gas with chlorine dioxide as a whitener for

bleaching and Alberta kraft mills switched to ECF bleaching approximately a decade ago (Grant, 2000).

Table 2-1 Summary of basis for mill discharge limits (after Nagendran *et al.*, 1995)

Substance	Limit
AO _x (kg/ADMT*)	0.8-1.5
Colour (kg/ADMT)	90**
2,3,7,8-dioxin & furan (ppq)	15 & 50

*ADMT = air dried metric tonne (of pulp)

** = monthly average limit

Elemental Chlorine free bleaching accomplishes the following (Pryke, 2001):

- (1) reduces 2,3,7,8-TCDD and 2,3,7,8-TCDF to non-detect levels;
- (2) decreases chloroform formation; and
- (3) decreases adsorbable organic halide (AOX) formation by 90%.

At a chlorine usage of about 44 kg/tonne of pulp, the AO_x is generated at a level of approximately 4.4 kg/tonne of pulp. That is, about one tenth of the chlorine becomes organically bound. As chlorine dioxide (D) is substituted for chlorine (C), there is a rapid reduction in polychlorinated phenols and dioxins (Solomon *et al.*, 1993). The significant fact is that the substitution reduces environmental loadings of

organochlorines. Nevertheless, because of the large volumetric effluent discharges of pulp mills, even with ECF bleach plant processes using chlorine dioxide, a typical pulp mill still produces 6 to 9 tonnes of organochlorines each day.

Organochlorines are mainly released in the form of chloroform (CHCl_3) which is known to be a carcinogen in animal studies (Solomon *et al.*, 1993). This undesirable outcome has prompted the mills to reduce the amount of chlorine of any kind used in the bleaching process. While TCF bleaching has not been widely adopted, extended digestion and oxygen delignification have proven to be economical ways to reduce the amount of chlorine required to produce a strong bright pulp. The oxygen delignification will be further discussed in Section 2.2.4.

2.2 Colour Causing Compounds

2.2.1 Sources

It is necessary to know which manufacturing process lines in a pulp mill are the main contributors of colour-causing compounds, in order to help understand colour characteristics and to determine colour removal methods. Among others, the wood pulp washing and kraft bleaching processes are the sources of most of the colour in the effluent because of their high water use and high colour loadings. Rush and Shannon (1974) reported that about 70% of the colour originates in the extraction stage, after the first of the bleaching operations. During pulping, lignin is dissolved

by appropriate chemicals to separate it from fibres and prepare the pulp for the subsequent bleach processes. During the pulping process, the lignin undergoes changes, which produce thioglignin and alkalilignin. It is reasoned that chromophoric (colour-causing) groups are intact lignin and lignin in forms modified by pulping and bleaching process.

2.2.2 Characteristics of Colour Causing Compounds

In spite of much effort, specific chromophoric groups contributing to colour have not been clearly identified. The dark brown colour of pulp mill effluent mainly comes from lignin and its derivatives. The lignin has not been precisely defined; yet it is described as highly branched (cross-linked) aromatic rings with a sub-unit molecular weight of about 840 (Rush & Shannon, 1974).

Falkehag *et al.* (1966) showed that the chromophores contributing to colour might be carbon-carbon double bonds conjugated with aromatic rings. Figure 2-3 shows an example of basic lignin structures in kraft liquor. Colour intensity in pulp mill effluent increases when pH increases. The shift of colour intensity is attributed to a change in quinoid structures in the effluent. Effluent colour precipitation has been found to occur at pH 3 and results in a decrease in colour intensity (Marton *et al.*, 1969). It is accepted that humic substances known to be colour-causing compounds are negatively charged (Hongve *et al.*, 1999). Therefore, their electrical charge may be considered a factor in developing a colour removal strategy.

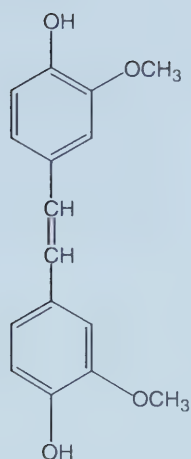


Figure 2-3 Example of basic lignin structures in kraft liquor, 4,4'-Dihydroxy-3,3'-dimethoxystilbene (after Falkehag *et al.*, 1966)

The molecular weights of the lignin fragments contributing colour are distributed over a broad range. This fact gives rise to difficulties in removing the molecules as well as in interpreting the removal mechanism (Rush & Shannon, 1974). Rush and Shannon (1974) found that bleach plant effluents contain lower molecular weight coloured compounds than found in strictly pulp stage streams owing to the further degradation of lignin that occurs during bleaching. Furthermore, intermediate molecular weight compounds having an average molecular weight of 5,600 make up the majority of the colour.

2.2.3 Effects of Colour

Although it is believed that the colour causing compounds in pulp mill effluent do not directly harm humans, Odendahl (1994) listed some of the effects on the environment caused by these compounds. These include an increase in potential nutrients for algal or bacterial growth in the river, and higher chlorine demand in drinking water treatment. Perhaps more importantly, the colour-causing humic substances derived from lignin can be precursors of mutagenic compounds after chlorination in drinking water (Santos & Duarte, 1998).

2.2.4 Removal Technologies

Since colour bodies derived from lignin are biologically stable, they are hardly degraded in biological treatment while readily biodegradable compounds, as quantified by BOD₅, can be very effectively removed. Therefore, several physicochemical treatment systems have been investigated. These include precipitation, ion exchange, activated carbon adsorption, ozonation, and membrane processes.

Rodriguez (1998) revealed that ozone can effectively degrade organic matter including colour-causing compounds. However, the effect of ozonation is not to completely degrade many of these compounds, but to reduce their molecular complexity and increase the BOD₅. Ultrafiltration and reverse osmosis have been employed to treat pulp mill effluent from the extraction stage and have shown high

colour removal efficiency (Rush & Shannon, 1974). These membrane processes are high pressure and energy-intensive systems that separate dissolved molecules from water. Therefore, these membrane processes require high capital and operating costs. Chemical precipitation using lime, iron, aluminium and polyelectrolytes can also remove colour but generate a considerable amount of sludge that must be disposed of (Odendahl, 1994).

Adsorption using activated carbon is capable of removing colour-causing compounds. However, because colour causing compounds are relatively large molecules, pore size of this adsorbent may inhibit the diffusion of colour causing compounds within the activated carbon pores and considerably reduce the available adsorption surface area. Pretreatment for AC adsorption is essential to treat pulp mill effluent, which is composed of a lot fibres and lignin. Regeneration of AC must be developed in economically effective manner. Unless the regeneration is accomplished, discarding significant amount of waste generated in the treatment cannot be avoided (Rush & Shannon, 1974).

Rather than relying on end-of-pipe treatment, much attention has been focused on reducing pulp mill contaminants in plant. Oxygen delignification technology can lead to less BOD and colour in the effluent as well as a reduction in the requirement and cost of chemicals (Argyropoulos, 2001). The move toward oxygen delignification was prompted by research conducted by Almberg (1980) who reported oxygen delignification has potential for reducing costs and pollutants. This research

suggested two possible new sequences that include oxygen delignification prior to the bleaching process (see Figure 2-1). These sequences are O-CEDED which uses oxygen delignification prior to the standard bleach sequence, and O-C/DEDED in which part of the free chlorine in the first bleach stage is replaced with chlorine dioxide. They mentioned that the determinant for this modified sequence is whether existing chlorination stage is likely to use chlorine dioxide. Table 2-2 is a list of summarized benefits when converting a 460 tonne/day bleach plant to O-C/DEDED (Almberg *et al.*, 1980).

Table 2-2 Results of converting 460 tonne/day bleach plant to O-C/DEDED (after Almberg *et al.*, 1980)

Effluent reductions (%)		Operating costs (\$/ton pulp)	
Volume	24	Chemicals	-10
Lignin	50	Water	-0.77
COD	45	Direct energy	-0.11
Colour	70		

According to the study conducted by Almberg *et al.* (1980), oxygen delignification was able to achieve 50% lignin reduction and 70% colour reduction in bleach plant effluent. In addition, this advanced technology is purported to save \$2.2 to \$4.4/tonne of pulp. Berry (1991) confirmed this earlier study, and concluded that

extended delignification (extended digestion), oxygen delignification, and better brownstock washing to lower lignin content into the bleach plant could accomplish as much as 50% lignin content reduction with respect to that produced in conventional pulping. Odendahl (1994) summarized the available advantages as follows:

- (1) lowering operating cost than strictly ClO_2 or Cl_2 bleaching;
- (2) reducing BOD_5 by 50% and colour by 60 %; and
- (3) reducing bleach plant chemical requirements.

On the other hand, oxygen delignification has low flexibility to increased load in evaporator and recovery boiler. Oxygen attacks fibre and produces weak pulp. While magnesium is generally added to the oxygen delignification stage to protect fibre against oxidation, this constraint limits the amount of colour that can be removed by oxygen delignification.

2.3 Chloride

2.3.1 AO_x and Chlorate Effects on the Environment

Chlorine containing chemicals are essential to the bleaching process in current pulp and paper mills. However, the chlorine might be bound to organics and form AO_x . AO_x is likely to pose risks to the environment and human health. Due to the toxicity of some halogenated organic compounds, AO_x is a frequently regulated parameter in pulp mill effluent (Folke, 1991). The persistence of AO_x leads to its accumulation

and biomagnification along the food chain. The rest of the chlorine is discharged in the form of inorganic chloride. The second North Sea Conference that was held in London in 1987 recommended a goal of the reduction of the discharge of hazardous substances via rivers by 50% over the next 10 years. The substances include persistent halogenated compounds from pulp and paper mill effluents such as AO_x and dioxins.

Sodium chlorate is the most frequent precursor shown in scheme (2-1) (Folke, 1991) for chlorine dioxide for elemental chlorine free (ECF) bleaching.



Chlorate is a frequently used herbicide. The discharge of substantial amounts of chlorate from a bleach plant may affect some macro-algae and the functioning of the whole ecosystem (Folke, 1991). Its effect on the human population is as yet unknown.

2.3.2 Effects on the Mill Itself

The effect of chloride and other dissolved NPEs on the mill infrastructure can be very detrimental. Precipitated chloride can cause corrosion on the wall of flue gas vents and the reduction of melting points in recovery boilers. This problem requires boilers to be shut down and washed as often as every three months (Brown *et al.*, 1999).

Along with the shut-down of the recovery boiler, the deposits can also cause loss of production which translate into major revenue losses (Rapp & Pfromm, 1998).

Due to the high solubility of chloride, it accumulates during the kraft pulping process. Brown liquor produced from the pulping process is sent to kraft chemical recovery system. High concentration of chlorides in the liquor make-up water will increase corrosion in the recovery boiler precipitators if the temperature of the equipment surfaces falls below the water vapour dew point of the flue gases. The condensed mixture of hydrochloric and sulphuric acids formed from flue gases will bathe the metal surface around flue gas vent (Sharp, 1996). In particular, coastal mills operating with brine water require special design for recovery boilers and treatment for process water to avoid high corrosion costs.

2.3.3 Progressive System Closure

Progressive system closure focuses on gradually reducing total effluent to the rivers with the goal of ultimately attaining zero effluent discharge. Wastes containing contaminants are discarded. Melanson (2000) reported that H.A. Simons (1994) indicated that the trend in modern mills is toward a reduction in the amount of water used and that the newest mills consume $61 \text{ m}^3/\text{ADMT}$. This result could be achieved by better washing efficiency, recycle of streams, and advanced removal technologies to treat effluents from various streams. Even if the zero effluent discharge goal were attained, fresh water in the amount of $19 - 24 \text{ m}^3/\text{ADMT}$ would still be needed to

make up with water loss, usually occurring as evaporation. The strategy can produce the following benefits:

- increasing water recycle;
- increasing chemical recycle;
- reducing or preventing problems such as corrosion and scaling; and
- minimizing the environmental impacts on pulp mill effluent.

The Rapson-Reeve Salt Recovery Process (SRP) was employed at Great Lakes Forest Products in Thunder Bay Ontario in the 1970's. It was the first kraft mill to attempt system closure. The SRP included a two-stage process of evaporation and crystallization to recover NaCl. The first stage concentrated the white liquor and then crystallized the Na_2CO_3 and $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. These were then removed by clarification and filtration. The second stage further concentrated the white liquor and crystallized NaCl. This process faced a number of problems, such as the corrosion of the white liquor evaporators (Melanson, 2000).

Melanson (2000) reviewed that Thompson *et al.* (1995) reported a three-compartment Bipolar Membrane Electrodialysis (BME) cell to remove chloride. This approach separates the NaCl in the electrostatic precipitator (ESP) dust into NaOH and HCl. Thompson *et al.* (1995) achieved removal of as much as 60% of the initial chloride concentration using this process.

Rapp and Pfromm (1998) achieved the selective removal of chloride from a high ionic strength solution containing multiple divalent anions, using electrodialysis with monovalent selective ion-exchange membranes. During the batch desalination tests, no membrane fouling was observed when 61% chloride removal was achieved.

Kahmark and Unwin (1999) reported that a compact, skid-mounted system using ion-exchange columns was capable of removing 90 to 99% of the chloride from various sources including dissolved ESP catch, oxidized white liquor, spent bleach scrubber liquors, spent ion-exchange demineralizer regenerants, and caustic soda makeup.

Millar Western's Meadow Lake pulp mill has been operated since February 1992. The mill produces hardwood bleached chemi-thermomechanical pulp (BCTMP) with zero liquid effluent. The hardwood pulp at the mill is TCF bleached, using an alkaline peroxide process (APP). An ion chromatograph has been used for tracking chloride in order to prevent corrosion and scaling. This mill has a modified recovery boiler which is designed to deal with the mill's sodium-based concentrate. All dissolved wastewater solids are incinerated in the recovery boiler. Its smelt and precipitator ash serve as the purge for inorganic salts. Meadow Lake is a good example of performing a mill closure system through modification and improvements in the mill processes (Meadows, 1996).

Progressive system closure in a kraft mill might cause the concentration of chloride and potassium in white and green liquor and lowering the melting point of dust deposits on recovery boiler superheater tubes. Hence, close monitoring is necessary for surface temperature of superheater tubes to remain below the first melting point of the deposits on these tubes (Sharp, 1996).

2.4 Ion-Exchange

2.4.1 Ion-Exchange Resins

Ion exchange is a physical-chemical process where aqueous ions transfer to exchange sites on resins through a liquid phase. Ion-exchange resins can be classified into cationic or anionic resins depending on whether the resins have positive or negative ions on exchange sites. Here only anionic resins will be discussed because they are promising for the removal of the colour-causing compounds and chloride.

Most ion exchange resins are manufactured as copolymers of styrene and divinylbenzene (DVB). The styrene frames the basic resin structure while the DVB crosslinks the polymers determining the internal pore structure.

Depending on functional groups, anionic resins are divided into strongly basic anionic (SBA) or weakly basic anionic (WBA) resins. SBA resins contain quaternary ammonium groups, while WBA resins have primary, secondary, or tertiary amines

(Montgomery, 1985). SBA resins are classified into type I and II, as shown in Figure 2-4, depending on the functional groups. The available functional group of type I resins is composed of three methyl groups attached to the quaternary ammonium. On the other hand, the functional group of type II consists of an ethanol group that replaces one of the methyl groups.

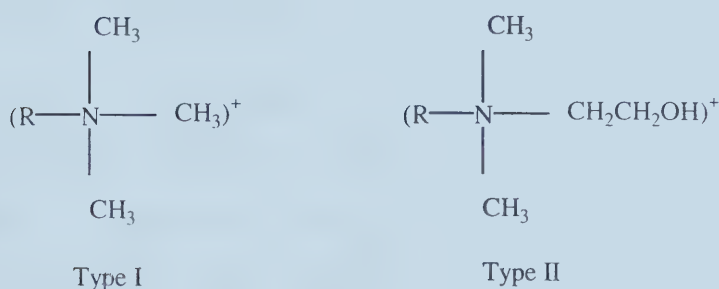
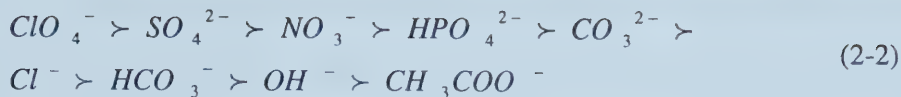


Figure 2-4 Type I and II functional groups (after Montgomery, 1985)

2.4.2 Selectivity

The ions to be removed compete with other components in a solution so as to take over positions on the exchange sites of resins. Such a process is affected by valence and concentrations of ions. Selectivity is defined as a resin's preference for one ion over another and is an important factor in selecting exchange resins. Scheme (2-2) below shows the selectivity of SBA resins among diverse anions (Clifford *et al.*, 1986).



This sequence is the same for WBA resins except that hydroxide is the most preferred ion. For this reason, WBA resins can not be utilized to treat streams containing high concentration of hydroxides when other ions other than hydroxide are to be removed, since hydroxide ions out-compete the other ions (Clifford, 1986). Generally, at low concentrations exchange affinities of multivalent ions increase with increasing valence of the exchanging ions. Chloride ion is monovalent and has relatively low affinity to anionic resins compared to other ions as shown in scheme (2-2). Therefore, a good chloride removal indicates that other anions, which have more affinity to resins than chloride, are removed to an even greater extent.

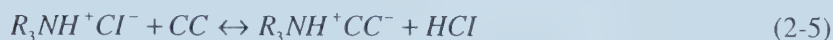
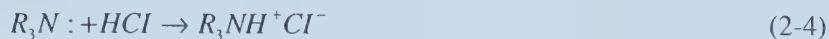
2.4.3 Colour Removal Schemes

SBA resins have been used for water demineralisation for decades. The quaternary ammonium functional group $[-N(CH_3)_3^+]$ allows SBA resins to be ionised over a pH range of 1 to 13. Scheme (2-3) shows that colour is removed from water by SBA resins in chloride form (Pontius, 1990):



where R is resin matrix or functional group such as $-CH_3$, $-C_2H_5$, and CC is a colour-causing compound.

WBA resins are used in the acidic pH region, where the primary, secondary or tertiary amine functional groups are protonated and can then behave as positively charged sites for anions. Chloride can be absorbed as a hydrochloric acid shown in (2-4). Positively charged R_3NH^+ provides the oppositely charged ion at the exchange site (2-5) (Pontius, 1990).



There are a variety of commercially available resins. The majority of the anionic resins are in the form of chloride and can be operated in a chloride cycle where the resins are regenerated with NaCl. If a hydroxide cycle is required, NaOH will be used as a regenerant.

In order to determine how well resins exchange ions to be removed, isotherm equations, developed to describe equilibrium conditions of adsorption, can be applied to the ion exchange process at equilibrium even though the ion exchange mechanisms are different from those involved in adsorption. The two most commonly applied isotherm equations are the Freundlich and the Langmuir equations. These isotherm equations are able to indicate the exchange capacities of resins, which are the most important characteristic. The characteristic is determined by the isotherm equations using the equilibrium relationship of ions between solid (resins) and solute phases at constant temperature. The resin exchange capacity is commonly

well expressed by the modified Freundlich equation given in (2-6) (Pontius, 1990). In the case of colour removal, the concentration of the solute can be expressed in terms of true colour units (TCU). K_F is known to be related to resin capacity of the ion exchange resins for ions to be removed.

$$\log\left(\frac{x}{M}\right) = \log K_F + \frac{1}{n} \log C_e \quad (2-6)$$

where:

x = colour adsorbed (TCU),

M = mass of resin (M/L),

C_e = liquid concentration at equilibrium (TCU/L),

K_F = Freundlich constant, and

n = Freundlich exponent.

The modified (linearised) Langmuir equation, (2-7), applied to colour exchange by resins is given by (Pontius, 1990):

$$\frac{C_e}{\left(\frac{x}{M}\right)} = \frac{1}{\left(\frac{x}{M}\right)_{\max} \bullet b} + \frac{C_e}{\left(\frac{x}{M}\right)_{\max}} \quad (2-7)$$

where, C_e , x , and M are as defined for the Freundlich equation. $(x/M)_{\max}$ and b are constants.

For a given resin, the most important factor determining the effluent concentration is empty bed contact time (EBCT) in the exchange columns calculated by (2-8) (Pontius, 1990):

$$EBCT = V_R / Q_F \quad (2-8)$$

where:

V_R = resin bed volume including voids (L^3), and

Q_F = volumetric flow rate (L^3/T).

The EBCT is related to the average fluid detention time in the column voids and is proportional to the length of the column.

2.4.4 Related Works with Ion-Exchange

Various ion-exchange processes have been implemented in full-scale. The Uddeholm-kamyr system used in Sweden has treated effluent from the initial caustic extraction stage characterized by a colour of 14,000 ppm (1 ppm = 1 TCU), BOD of 800 ppm and a COD of 2,400 ppm. It has been shown to achieve 90% colour removal with BOD and COD reductions of 50% and 80%, respectively (Lindberg, 1973). Three ion exchange schemes: the Dow process, the Rohm and Haas process, and the Billerud Non-Polluting Bleach Plant Concept, have been designed to treat pulp and paper mill effluent for the purpose of minimizing chemical and pollutant disposal costs. The Billerud systems illustrated that WBA resins of a phenol-formaldehyde matrix were effective for treating the mill effluent under acidic

conditions ($2 < \text{pH} < 4$) (Fitch, 1985). Lindberg and Lund (1980) estimated that energy costs in the Billerud system could be reduced to half of that of an aerated lagoon.

Kolle (1979) and Brattebo *et al.* (1987) investigated ion exchange using a SBA resin named Lewatit MP 500A to treat high-colour groundwater. Treatment with the macroporous resin removed 58% of the organic carbon. In addition, the exhausted resins were successfully regenerated with a 100 g/L NaCl and 20 g/L NaOH solution (Kolle, 1979). Brattebo and coworkers (1987) derived isotherm parameters and an empirical model for breakthrough curves of humic acids for the Lewatit MP 500A resin. The operating parameters for running columns such as EBCT, initial colour concentration in an influent to columns, and reusable amount of regenerant have been determined.

3 Materials and Methods

3.1 Materials

3.1.1 Ion-Exchange Resins

Nine ion exchange resins were purchased from Sigma Chemical Co (Oakville, Ontario). Of these, two were WBA resins including Amberlite® IRA67 and IRA92 and seven were SBA resins including Amberlite® IRA400, IRA402, IRA458, IRA900, IRA958, IRN78, and Amberjet® 4400OH. These nine resins were selected based on the previous study in my laboratory and the information provided by Rohm and Haas Inc (2000). Grant (2000) recommended IRA400, IRA410, IRA67 and IRA900 for colour removal and the other resins were suggested by the resin manufacturer. These resins were stored at room temperature. General information regarding each resin, provided by Rohm and Haas Canada Inc (2000), is summarized in Table 3-1. IRA67, IRA458, and IRA958 have an acrylic DVB matrix structure and other six resins have a styrene DVB structure. According to the manufacturer, all of SBA resins can be operated in the whole pH range of 0 to 14 while the two WBA resins must be operated in the pH range of 0 to 7.

For all absorbance readings in colour measurement, a Hewlett-Packard 8453 UV-Vis spectrophotometer interfaced with a Seanix computer was used.

Table 3-1 Ion-exchange resin characteristics (after Rohm Haas, 2000)

Resin name	Resin form & porosity	Matrix	Functional group	Ionic form	Capacity (meq/mL)	pH range
Amberlite IRA67	WBA, Gel	Acrylic - DVB	Tertiary Amine	Free base	1.6	0-7
Amberlite IRN78	SBA, Type I Gel	Styrene - DVB	Quaternary Ammonium	OH ⁻	1.2	
Amberlite IRA92RF	WBA, Macroporous	Styrene - DVB	Tertiary Amine	Free base	1.6	0-7
Amberlite IRA400	SBA, Type I Gel	Styrene - DVB	Quaternary Ammonium	Cl ⁻	1.4	0-14
Amberlite IRA402	SBA, Type I Gel	Styrene - DVB	Quaternary Ammonium	Cl ⁻	1.3	0-14
Amberlite IRA458	SBA, Type I Gel	Acrylic - DVB	Quaternary Ammonium	Cl ⁻	1.25	0-14
Amberlite IRA900	SBA, Type I Macroporous	Styrene - DVB	Quaternary Ammonium	Cl ⁻	1	0-14
Amberlite IRA958	SBA, Type I Macroporous	Acrylic - DVB	Quaternary Ammonium	Cl ⁻		0-14
Amberjet 4400OH	SBA, Type I Gel	Styrene - DVB	Quaternary Ammonium	OH ⁻	1.1	0-14

A Fisher vacuum pump was used to filter solutions in colour measurement. The platinum- cobalt colour standard solution and chloride standard solutions of three different concentrations of 100, 1,000, and 3,550 ppm were purchased from Fisher Scientific, Canada. The platinum-cobalt colour standard solution was stored at 5°C and chloride standard solutions were kept at room temperature. For chloride measurement, a Fisher Scientific Accumet 50 pH meter was used with an Orion 96-17B Combination Chloride Electrode. The electrode was purchased from Orion Research Inc.

3.1.2 Sample characterisation

Samples of kraft pulp mill effluent examined in this study were obtained from Weyerhaeuser Canada Ltd. in Grande Prairie, Alberta, Canada that uses no colour reduction technology except peroxide addition when high colour loadings occur. Samples were collected from the following locations within the plant:

- (1) Influent to aerated lagoon;
- (2) Effluent from aerated lagoon;
- (3) Acidic sewer from the bleach plant; and
- (4) Caustic sewer from the bleach plant.

The bleach plant operates with 100% chlorine dioxide bleaching (ECF bleaching). Samples were stored at 5°C.

The sample characterisation with respect to colour (TCU), chloride concentration (ppm), and pH is summarized in Table 3-2.

Table 3-2 Sample Characterisation

	Colour (TCU)	Cl ⁻ (ppm)	pH
Lagoon influent	890-930	250	7.4
D stage effluent	2710	740	2.3
E _{op} stage effluent	2670	300	11.4
Blended bleach wastewater	1200	190	6.5
Final effluent	920-1330	200-290	7.9

D stage effluent (acidic) is produced from the brightening stage in which ClO₂ is the main chemical used. The pH value of the D stage effluent was very low at 2.3. On the other hand, E_{op} stage effluent (alkali) was collected from an extraction stage in the mill. The pH value of the E_{op} stage effluent was very high at 11.4. The chloride concentration of the D stage effluent was twice that of the E_{op} stage effluent while the colour concentration of the D stage effluent was comparable to the E_{op} stage effluent.

The flows of the acidic and alkali sewers are blended and mixed with wastewater from the wash stages and the flow from the general (sanitary) sewer

before being introduced to an aerated lagoon. Therefore, it can be reasoned that the components in the lagoon influent are from the D and E_{op} stage effluents diluted by the many washing steps and general sewage prior to the biological treatment. Consequently colour and chloride concentrations of lagoon influent are much less than those of the D or E_{op} stage effluent. The pH values of both lagoon influent and final effluent are close to neutral. Aerated lagoon biological treatment is not able to remove colour other than by adsorption to floc particles. The differences in colour and chloride concentration may be caused by variation of sampling.

3.2 Methods

3.2.1 Colour Measurement and Colour Unit Conversion

Pulp mill effluent colour was determined by a standardized method of the Canadian Pulp and Paper Association (1974). For colour measurement, approximately 10 milliliters of sample were filtered through a glass fibre filter (Fisher G8 grade, cat. number 9-804-70D), and subsequently through a membrane filter (Millipore GT Type, Fisher cat. number GTTP 037 00) with the aid of a vacuum pump. The filtrate was then adjusted to a pH of 7.6 with hydrochloric acid or a solution of sodium hydroxide.

The absorbance was measured on a spectrophotometer at 465nm, and compared to the absorbance of a platinum cobalt colour standard solution. The standard solution indicates 500 total colour units (TCU). The colour of each sample

(in TCU) is proportional to absorbance of the sample as shown by the following (3-1):

$$TCU_{sample} = (500 \times A_{sample}) / A_{PtCo} \quad (3-1)$$

where:

A_{sample} = absorbance of the sample at 465 nm, and

A_{PtCo} = absorbance of 500 CU platinum-cobalt colour solution at 465 nm.

In some of the literature, colour concentration is expressed in other units other than TCU. The relationship given in (3-2) can be applied in order to convert TCU to mg Pt/L (Sawyer *et al.*, 1994).

$$1 \text{ TCU} = 1 \frac{\text{mgPt}}{\text{L}} \quad (3-2)$$

3.2.2 Chloride Measurement

The method to measure chloride was instructed by the manual of electrode provided by Orion Research, Inc (2000). For chloride measurements, one milliliter of ionic strength adjuster (ISA) and five milliliters of Chloride Ionic Strength Adjuster (CISA, 1.0 M Nitric Acid) were added to 50 milliliters of sample. CISA, an oxidizing agent, is added to minimize interference to the chloride measurement by oxidizing up to 500

mg/L S^{2-} , 100 mg/L Br^- or I^- , 100 mg/L NH_3 , or a 100-fold excess of CN^- over Cl^- (Orion Research, 2000).

Chloride standards of known concentration were also prepared in the same manner, and a calibration curve was created by plotting chloride concentration as a function of mV. The equation of the resulting trace was used to determine the chloride concentration of samples based on their mV measurement.

3.2.3 Batch Experiments

For the investigation of the effects of resin doses on both colour and chloride removal, resin doses of 0.2, 1, and 3 g per 100 mL of sample were used. Sample and resin were placed in 125 mL vials and mixed using a stir bar propelled by a magnetic stirrer in order to allow resins to evenly contact samples. Each batch test was run for a 24 hour period to allow the exchange process to reach equilibrium.

For regeneration studies with blended bleach wastewater, samples were prepared by blending D : E_{op} : deionised water at the ratio of 1 : 1 : 4. 1 N NaOH in combination with 1 N NaCl was prepared in the ratio of (40 g NaOH and 58.5 g NaCl)/1L of deionised water. 100 mL of regenerants per a vial was used.

For each isotherm test, 250 mL Erlenmeyer flasks were used rather than vials. Each Erlenmeyer flask was filled with 100 mL of sample. The equilibrium study

using IRA900 and IRN78 for colour and chloride removal was conducted at the resin dose of 10 g/L.

For the colour isotherm studies, resin doses of 2, 4, and 6 g/L were added to 100 mL of sample. For the chloride isotherm studies, resin doses of 4, 10, and 25 g/L were added to 100 mL of sample. In order to prevent resins from being broken by the action of the magnetic stirring bars, a shaker was employed because it does not require stirring bars for mixing. The shaker was set to 250 RPM to provide enough rotational speed for homogeneous mixing. Resins were thoroughly rinsed with deionised water after regeneration to prevent residual regenerant affecting the next colour removal. Filter papers supported by funnels were used. All of the isotherm tests were performed at a constant temperature of 20°C.

3.2.4 Column Experiments

The single fixed-bed column experiments were performed using a 40 cm high and 1.9 cm inner diameter down-flow loaded minicolumn (Knotes Brad Adsorption/Ion exchange column, K420320-0224). During initial column tests using final effluent, clogging of the columns was observed. Therefore, final effluent sample was pretreated by filtration to minimize clogging of the column thereafter. This involved filtering the final effluent using 2.5 µm and 0.3 µm glass fibre filters before use.

Resin was loaded into each column to a depth of 20 cm, the column was filled with water to just above the surface of the resin bed, and the resin was packed gently using a bar to press down the resin. Air bubbles were observed to be released from the resin bed and rise to the water surface when doing so. The presence of air bubbles could reduce the available flow paths through the resin bed and promote clogging during operation. In fact, clogging occurred quickly when a column was put into operation immediately after being packed. Therefore, after being packed with resin, columns were allowed to stand for at least one day before being used, to prevent the columns from clogging during operation. At the end of this period, approximately 3 cm of glasswool was placed above the resin beads to retain them. Allowing the columns to stand for a day or more and filtration of the final effluent sample seemed to solve the clogging problem and ensure relatively stable flowrates through the column during operation.

Each run of the breakthrough studies was stopped when the concentration in the column effluent reached half of influent concentration. The diagram of the continuous flow system is shown in Figure 3-1. Sample was input by a peristaltic pump to the top of column and allowed to flow down through the resin bed. Samples were collected at the column outlet. The designed operating parameters for column testing are given in Table 3-3.

For determining elution curves, tests were stopped as residual concentration of the effluent at the outlet over the initial of colour or chloride reached 0.3. The resin

was then regenerated. During each run samples were collected at a constant time intervals. The column testing was designed such that colour removal took place in the first column and chloride removal occurred in the second column. For chloride breakthrough and elution studies, the effluent from colour removal column was input to the chloride column. Sample, flowing out of the colour removal column containing IRA958, until C_e/C_0 of colour reached 0.1 was collected in a container. No colour in the collected sample was visually observed. The overall chloride concentration of the collected sample, which was the influent provided for the chloride column for both removal and elution, was determined to be approximately 510 ppm.

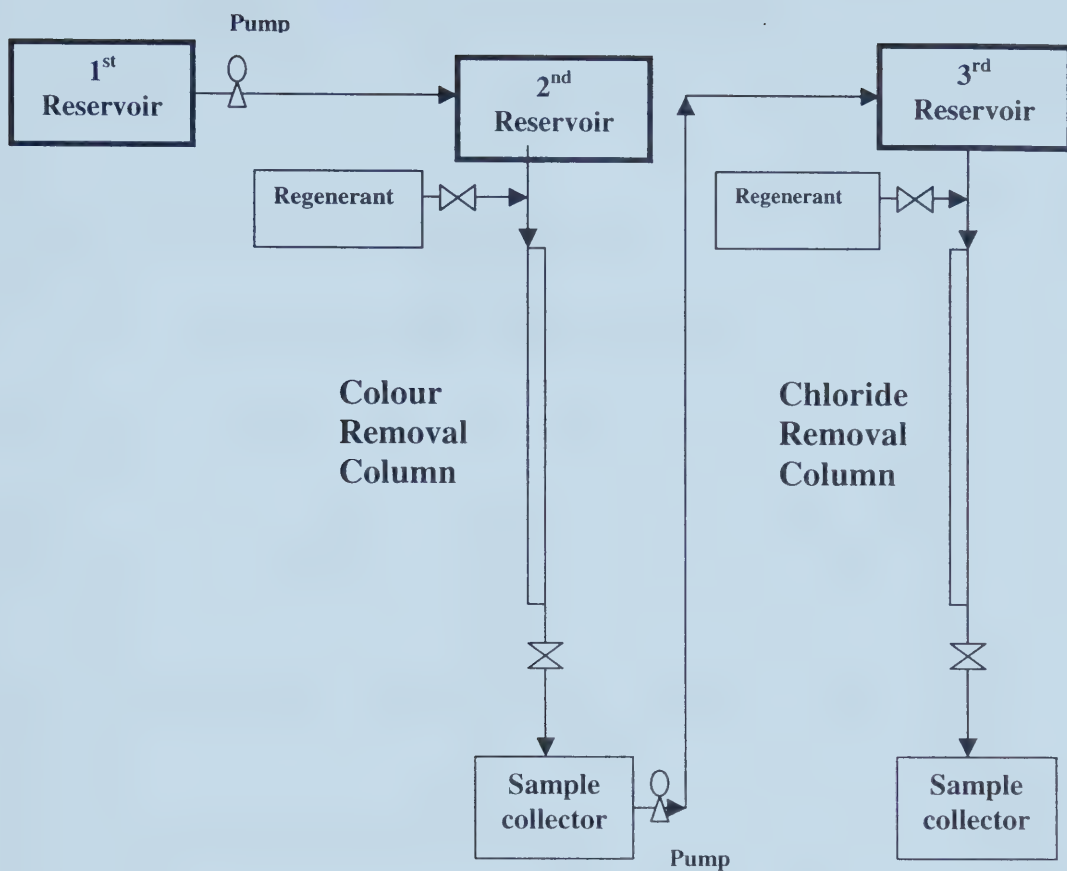


Figure 3-1 Continuous flow test diagram

Table 3-3 Continuous downflow column experiments

	Flowrate (mL/min)	Duration (min)
End of service run		
Backwash	3	10
Regeneration	3.8	10
Rinse	5	60

4 Results and Discussion

4.1 Colour Removal Batch Testing

4.1.1 Decolourisation with Different Resins

This testing was conducted to determine the effect of resin type and dose on colour removal. Colour removal from three types of samples including lagoon influent, D stage (acidic sewer) effluent, and E_{op} extraction stage (alkali sewer) effluent, was investigated using resin doses of 2, 10, and 30 g/L. The results of the colour removal tests for each effluent resin type and dose are shown in Figures 4-1, 4-2, and 4-3. No colour removal was observed in control vials containing effluent and no resin. Removal efficiency was calculated by equation (4-1).

$$\eta = \frac{C_o - C_e}{C_o} \times 100(\%) \quad (4-1)$$

where:

η : Removal efficiency (%),

C_o : Initial colour concentration in an effluent, and

C_e : Residual colour concentration after ion exchange.

Figure 4-1 illustrates that IRA958 treating lagoon influent showed approximately 97% colour removal at a resin dose of 2 g/L. IRA900 removed almost

all of colour at 30 g/L. IRN67 also reached 90 % of colour removal at 10 g/L and IRA92 removed 85% at 30 g/L. IRN78, IRA400 and 4400OH removed less than 50% of initial colour concentration of lagoon influent at the highest resin dose of 30 g/L tested. IRA402 showed modest colour removal of around 60% from the lagoon influent at 2 g/L.

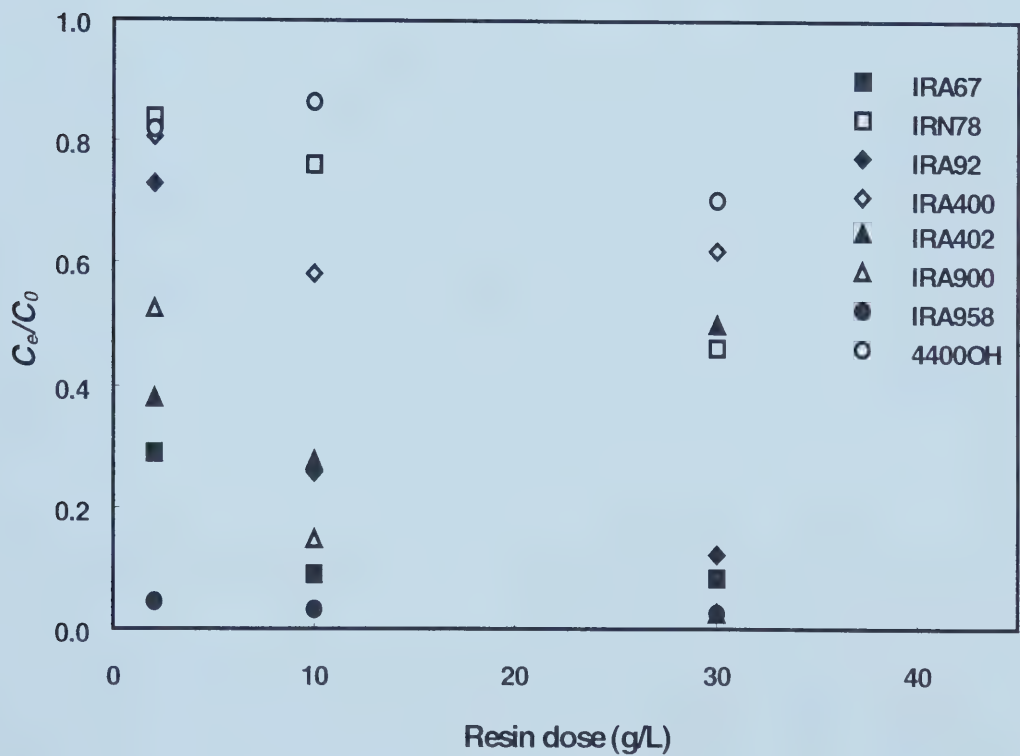


Figure 4-1 Decolourisation of lagoon influent by eight anionic resins (20°C, C_0 : 890 - 910 TCU, pH : 7.5 - 7.8, Contact time : 1 day)

Figure 4-2 shows that IRA958 achieved modest colour removal efficiency. IRA67, IRA92 and IRA900 showed better performance of colour removal than the others in treating the D stage effluent. As indicated in Figure 4-2, IRA400 and 4400OH did not have a good performance in removing colour from the D stage effluent. Removal with IRN78 and IRA402 improved with increasing resin dose but was not sufficient within the tested range.

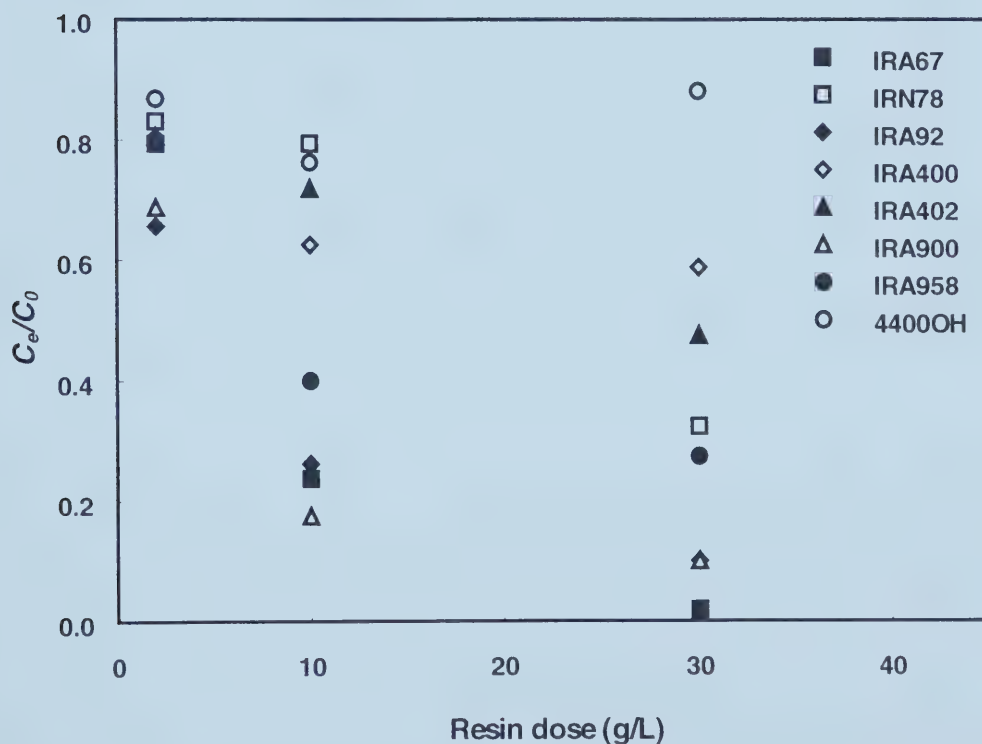


Figure 4-2 Decolourisation of D stage effluent by eight anionic resins (20°C, C_0 : 2550 - 2580 TCU, pH : 2.2 - 2.3, Contact time : 1 day)

In the decolourisation from the E_{op} stage effluent (see Figure 4-3), IRA900 and IRA958 had almost 90% removal efficiency at the resin dose of 30 g/L. IRN78, IRA92, IRA400, IRA402 and 4400OH performed fairly well. IRA67 could not remove any colour. Due to experimental error, the concentration after ion exchange seems higher than initial colour concentration of E_{op} stage effluent.

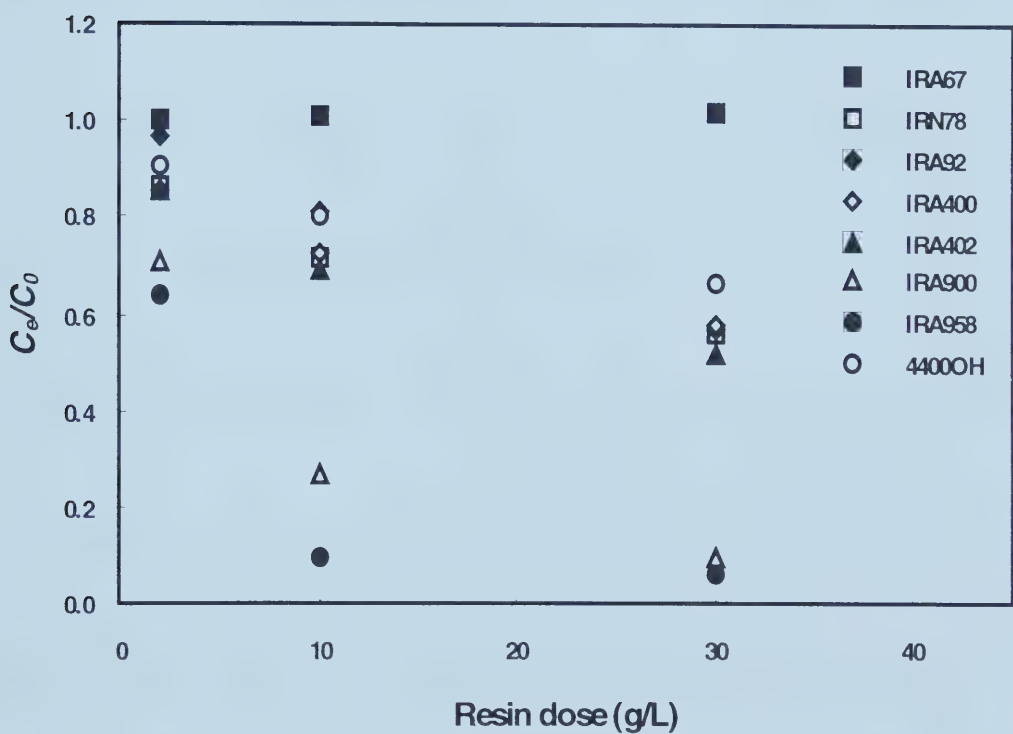


Figure 4-3 Decolourisation of E_{op} stage effluent by eight anionic resins (20°C, C₀ : 2620 - 2760 TCU, pH : 11.4, Contact time : 1 day)

Contrary to the results with lagoon influent (see Figure 4-1) and the E_{op} stage effluent (see Figure 4-3), IRA958 treating the D stage effluent (see Figure 4-2) did not produce the highest removal efficiency. The low pH of the D stage effluent might affect the ion exchange, or the stirrer used could not provide resins with enough mixing to let resins completely contact coloured effluent. Magnetic bars placed in vials broke some resin beads, particularly IRA900 which was being broken into fine powder in some vials. IRA900 did not seem to be resistant to the mechanical mixing.

Duplicates were prepared by placing the same amount of resin and effluent in two vials. Variation of colour removal between duplicates was quite considerable in cases where more resin breakage occurred in one vial than in the other. More colour removal was observed in the vials containing the broken resin beads than in the vials in which breakage did not occur. This may indicate that diffusion resistance due to the relative sizes of the colour causing compounds and resin pores is quite important. As indicated in Section of 2.2.2, the average molecular weight of colour causing compounds has been reported to be 5,600. Therefore, access of these large molecules to exchange sites located within the resin matrix may be limited by resin pore size.

Samples after decolourisation with IRN78 and 4400OH had high pH values. The final pHs of the three kinds of samples are shown in Tables A-1 to A-3 in Appendix A. These pH increases were due to the resins exchanging hydroxide ions for colour causing compounds.

The D stage and E_{op} stage effluent samples contained twice as much colour as the lagoon influent as shown in Table 3-2. Due to the difference in initial colour concentrations of the three samples tested, this may obscure the actual colour removal efficiencies of the resins. Therefore, it is instructive to review these data from the perspective of the number of TCU removed. The 2 g/L dose of IRA958 achieved almost the same removal from E_{op} stage effluent (35% of 2670 = 935 TCU) (see Figure 4-3) as it did from lagoon influent (97% of 910 = 883 TCU) (see Figure 4-1). The difference between the initial colour concentrations of the E_{op} stage and lagoon influent samples is due to dilution that the wastewater undergoes as waste streams from various points in the mill are blended. If this dilution can be calculated according to the difference in colour concentrations of the samples used in the present investigation, then a further reduction of $(1 - 910/2670) \times 100\% = 66\%$ can be expected for the treated E_{op} stage effluent. Thus, if the E_{op} effluent were treated with 2 g IRA958/L and this treated effluent subsequently underwent the expected dilution, the resulting colour in the lagoon influent would be $(2670 - 935) \times (1 - 0.66) = 590$ TCU. Therefore, it appears that application of colour removal by IRA 958 would be more efficient if applied to the lagoon influent which resulted in a final colour of approximately 27 TCU, and the representation of the results as fractional colour remaining is justified.

4.1.2 Regeneration Study

The objective of the regeneration study was to determine effective regenerants to release colour-causing compounds from the resins. In the regeneration study, two types of regenerants, NaOH alone and in combination with NaCl, were examined to regenerate exhausted resins. A regeneration study using NaOH was conducted on resins used to decolourise two types of effluents, final effluent from the aerated lagoon and blended (D-stage mixed with E_{op}) bleach plant wastewater. A regeneration study using the combined regenerant was conducted with resins that had been used to decolourise the final effluent.

Figure 4-4 represents the results from the regeneration study with 0.5 N NaOH at 10 g/L. The following six resins were tested: IRA67, IRN78, IRA92, IRA900, IRA958, and 4400OH. Three colour removal ion exchange cycles and two regenerations were conducted during this study. 1st in the graph stands for colour removal with virgin resins and 2nd or 3rd represents colour removal with resins which had undergone regeneration once or twice, respectively. Virgin IRA67, IRA900, and IRA958 achieved about 90% colour removal from final effluent. After exhausted resins were regenerated with 0.5 N NaOH, colour concentrations of the effluent after the 2nd and 3rd ion exchanges remained high, compared with that in the first colour removal cycle. Virgin IRA92 removed up to 50% of the colour, but removal efficiencies deteriorated with repeated regeneration trials. Virgin IRN78 and 4400OH achieved colour removal efficiencies of only 10 - 15%. In terms of

regeneration efficiency, 0.5 *N* NaOH was not capable of regenerating resins sufficiently. Regeneration efficiency was calculated by equation 4-2.

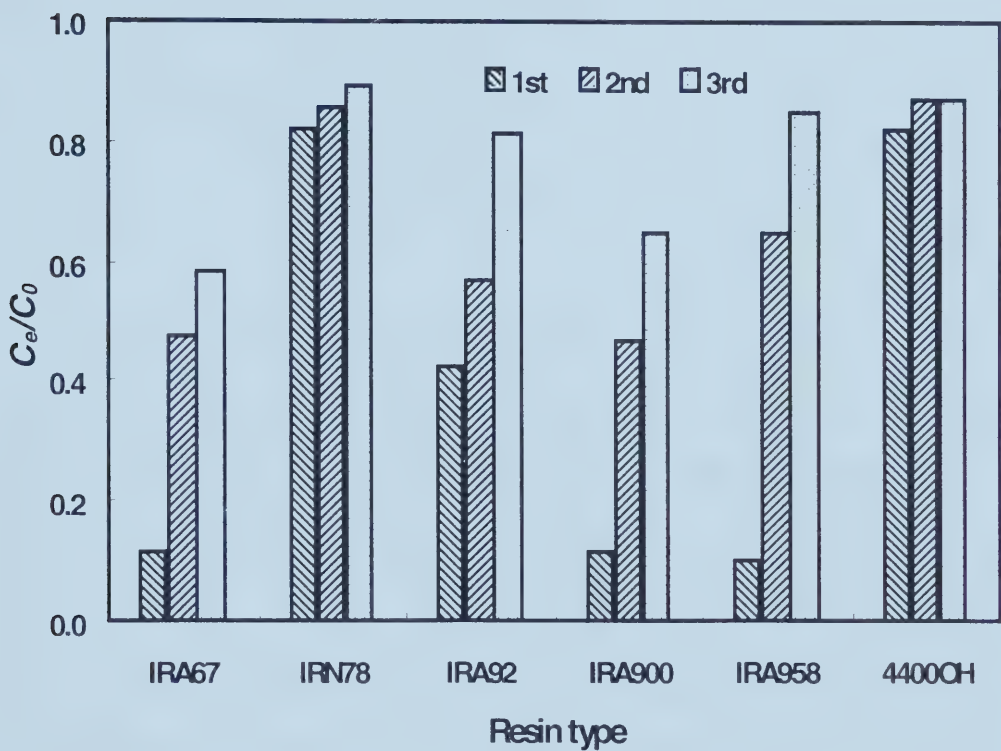


Figure 4-4 Regeneration using 0.5 *N* NaOH (21°C, Final effluent C_0 : 960 TCU, pH 7.9, Resin dose : 10 g/L, Contact time : 1 day)

$$\eta_R = \frac{C_0 - C_{R,e}}{C_0 - C_{e,1st}} \times 100(\%) \quad (4-2)$$

where:

η_R : Regeneration efficiency (%),

C_0 : Initial colour concentration in an effluent,

$C_{R,e}$: Residual colour concentration using regenerated resins, and

$C_{e,1st}$: Residual colour concentration using virgin resins.

Figure 4-5 contains results from the regeneration study which used the more concentrated regenerant of 1 *N* NaOH. The tests were conducted at the same resin dose of 10 g/L with the same sample (final effluent). IRA458 showed 80% of colour removal, but after regeneration the removal efficiency dropped to only 20%. Some resins experienced little improvement relative to regeneration efficiency obtained using 0.5 *N* NaOH. Data on colour removal with six virgin resins except IRA458 used from this study should be the same as in the previous trial (see Figure 4-4). However, the colour removal efficiency of IRA900 is remarkably different in Figures 4-4 and 4-5. This difference cannot easily be explained because both sets of tests were conducted under the same conditions (resin dose of 10 g/L, same kind of sample, and same temperature). Residual colour concentration after the first colour removal test with IRA900 in Figure 4-4 was 10% of the initial colour, but that in Figure 4-5 was almost 40% of initial colour concentration. This difference may result from broken resins. As the colour removal testing summarized in Figure 4-4 was

conducted, IRA900 was broken by a stirring bar and it may make IRA900 increase its available surface area and access to exchange sites.

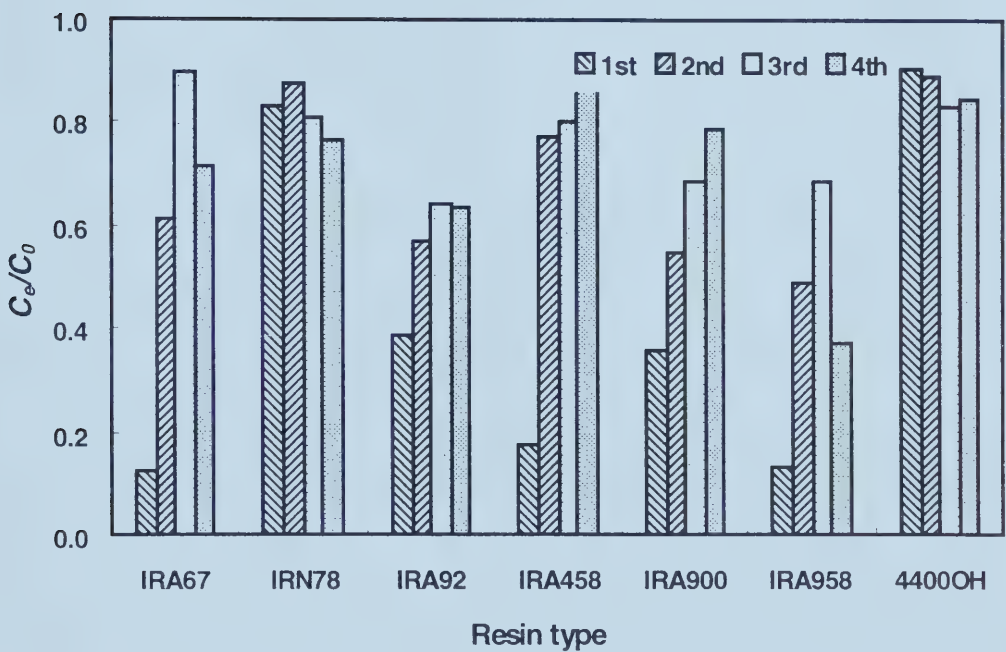


Figure 4-5 Regeneration using 1 N NaOH (21°C, Final effluent C_0 : 940 TCU, pH 7.8, Resin dose : 10 g/L, Contact time : 1 day)

Regeneration with either 0.5 *N* (see Figure 4-4) or 1 *N* NaOH (see Figure 4-5) could not show high regeneration efficiencies. Virgin IRA958, which performed best in the resin dose effect study and regeneration study had highest colour removal efficiency among resins tested. However, the removal stopped at around 50% after the first regeneration with 1 *N* NaOH compared to the 85% removal achieved by virgin IRA958 resin. These results indicate that NaOH alone is not an adequate regenerant for these resins (see Figure 4-5).

Figure 4-6 illustrates the results of the regeneration study with 1 *N* NaOH in terms of colour removal from blended bleach plant wastewater. Almost 98% of colour was removed by the virgin IRA458, IRA900, and IRA958 resins, but as was the case during the tests with final effluent (see Figure 4-5), residual colour concentration increased with increasing exchange-regeneration cycles. The WBA resins, IRA67 and IRA92 did not show good regeneration efficiencies. The regenerated IRA67 and IRA92 resins containing hydroxide ions on exchange sites might not easily lose the ions since the most preferred ion to WBA resins is hydroxide. Removal efficiency using the combined wastewater (see Figure 4-6) in IRN78 and 4400OH was better than that using final effluent (see Figure 4-5); yet, the two resins are not competitive with IRA900 and IRA958 in terms of colour removal efficiency.

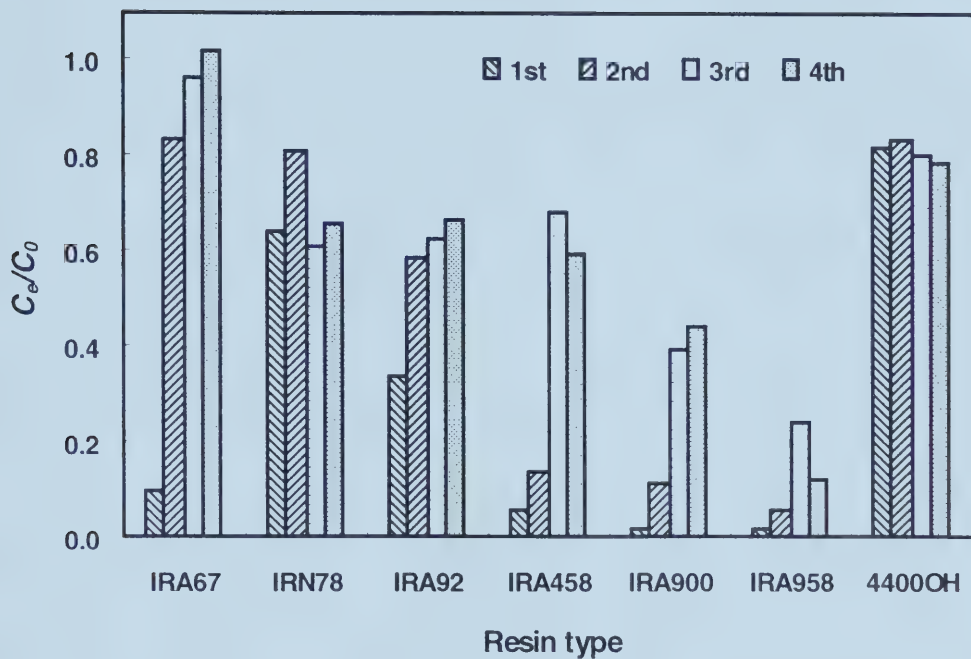


Figure 4-6 Regeneration using 1 N NaOH testing blended bleach wastewater (21°C, Blended bleach wastewater C_0 : 890 - 930 TCU, pH 6.5, Resin dose : 10 g/L, Contact time : 1 day)

At this point five types of samples had been tested for colour removal by ion exchange. These are: lagoon influent, final (lagoon) effluent, D stage effluent, E_{op} stage effluent, and the combined bleach plant effluent. The results indicate that the best colour removal was obtained from lagoon influent, final (lagoon) effluent, and the combined bleach plant effluent, when virgin IRA458, IRA900, or IRA958 were used. The amount of colour removed from D stage (pH 2.2) and E_{op} stage effluent (pH 11.4) per gram of resin supplied was somewhat less. This may be due to the effect of the extreme pH values of these two streams that reduce the resins' ion exchange abilities. Therefore, the process could be applied either to a blended bleach plant waste stream, just upstream of the lagoon inlet, or at its outlet using IRA458, IRA900, or IRA958 if a suitable regenerant were identified. Final effluent was chosen as the sole sample to be tested during the remaining colour removal tests in order to streamline the testing and because this wastestream is expected to require the least pre-treatment to render it amenable to treatment in ion exchange columns. Therefore, regeneration testing continued using final effluent and a regenerant consisting of 1 N NaOH and 1 N NaCl.

Figure 4-7 represents the results from using 1 N NaOH in combination with 1 N NaCl (40 g NaOH/L and 58.5 g NaCl/L of deionised water) to regenerate the three most effective resins: IRA458, IRA900, and IRA958 after colour removal from final effluent samples. The tests to remove colour from the final effluent were implemented at the three resin doses of 2, 10, and 30 g/L.

The results given in Figure 4-7 illustrate that IRA958 undergoing the first regeneration with the combined regenerant performed as well in terms of removal efficiencies as virgin resins and even slightly better. Virgin IRA958 removed more than 90% ($\pm 0.4\%$) of colour in final effluent at the resin dose of 10 g/L. IRA958 after the second regeneration achieved close to 100% ($\pm 0.5\%$) colour removal. IRA900 achieved a consistent removal efficiency of more than 90% through the three colour removal cycles at 10 g/L. IRA458 provided colour removal of approximately 70% in each colour removal period through all of three ion-exchange cycles at 10 g/L. It can be concluded that the ion exchange performance with all of the three resins after regenerations using 1 *N* NaOH in combination with 1 *N* NaCl did not decrease relative to virgin resin performance. In terms of regeneration efficiency, 1 *N* NaOH in combination with 1 *N* NaCl was very effective as a regenerant for all of three resins. IRA458, IRA900, and IRA958 were chosen to further investigate resin capacity in isotherm testing and column testing. More regeneration studies conducted using diverse ratios of NaOH and NaCl are given in Tables A-4 and A-5 in Appendix A.

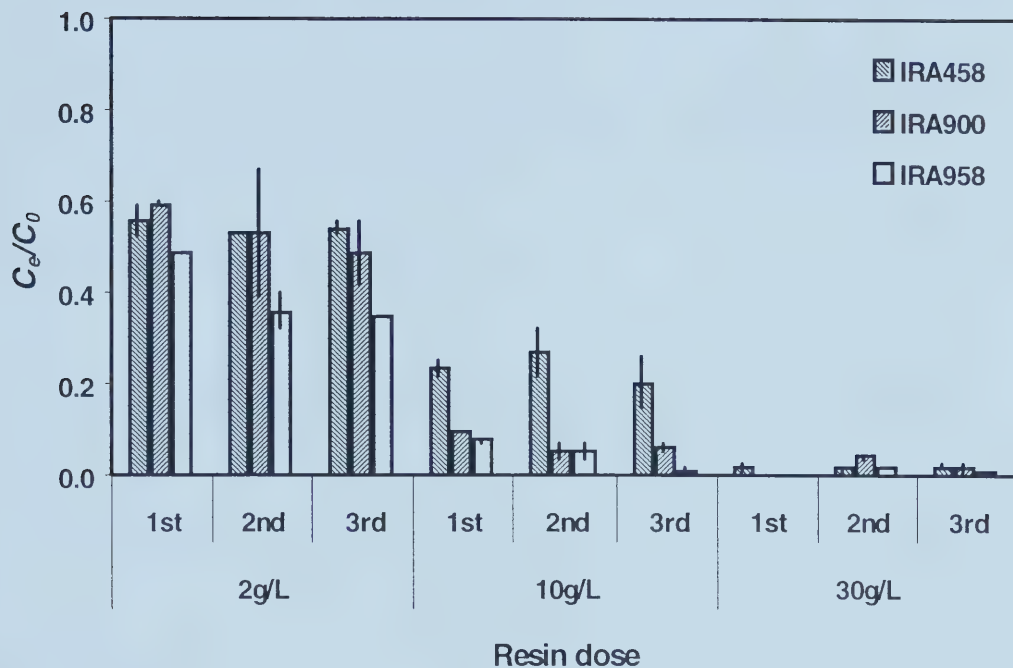


Figure 4-7 Regeneration using 1 *N* NaOH in combination with 1 *N* NaCl testing final effluent (18°C, Final effluent C_0 : 920 - 1230 TCU, pH 7.8 , Resin dose : 10 g/L, Contact time : 1 day). Note: 100% colour removal using IRA900 and IRA958 at the resin dose of 30 g/L.

4.1.3 Colour Isotherm Testing

The objective of the isotherm testing was to determine the best resin for colour removal based on resin exchange capacity. To obtain reliable results, a rotary shaker was substituted for the magnetic stirrer, which had caused resin beads to break during stirring. The colour isotherm tests were carried out at the resin doses of 2, 4, and 6 g/L, at a constant temperature of 20°C, and in duplicate.

Prior to the isotherm tests, preliminary equilibrium tests using IRA 900 for colour removal, and IRN78 for chloride removal, were conducted to determine the time required for equilibrium to be reached. Based on the observations shown in Table 4-1, equilibrium was reached after two and one days for colour and chloride removal, respectively.

Table 4-1 Results of equilibrium tests (Final effluent initial colour concentration: 1220 TCU, initial chloride concentration: 235 ppm, Shaker : 250 RPM, Resin dose : 10 g/L)

Test duration (Days)	Final colour (TCU)	Final chloride (ppm)
1	48	149
2	1	164
3	6	
Time to equilibrium	1 day	2 days

Residual raw data of colour isotherm testing shown in Table A-6 in Appendix A indicate IRA958 of the three outperformed the other two in terms of removal efficiency. Figure 4-8 represents Freundlich isotherm plots of three virgin resins including IRA458, IRA900, and IRA958. Freundlich isotherm graphs were linearised in logarithmic scale of residual colour concentration to a function of

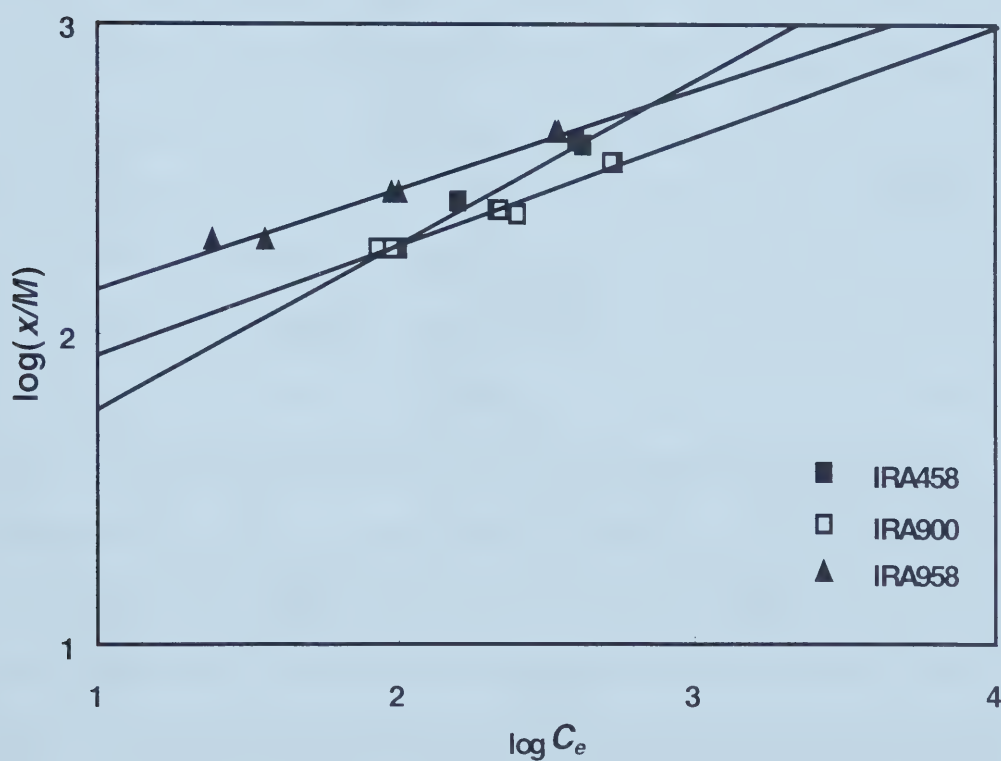


Figure 4-8 Linearised Freundlich isotherms for three virgin resins in colour removal (20°C, Final effluent C_0 : 1240 TCU, Shaker : 250 RPM, Resin dose : 2, 4, 6 g/L).

exchanged colour concentration divided by the quantity of resin for the ion exchange. It is reasonable to say that resins in lesser amounts removing more colour have high exchange capacities. Therefore, a high y intercept ($\log K_F$) (see 2-6 in Section of 2.4.3) means that the resin possesses a high resin exchange capacity. Therefore, Figure 4-8 demonstrates that virgin IRA958 had the higher exchange capacity compared with virgin IRA458 and IRA900.

Figures 4-9 and 4-10 represent Freundlich isotherms of resins after one and two regenerations, respectively. After the first and second regeneration with 1 *N* NaOH in combination with 1 *N* NaCl, IRA958 still exhibited the higher exchange capacity of the resins tested. The Freundlich parameters (K_F and n) of virgin and regenerated resins were calculated and are shown in Table 4-2. Resin capacity, as characterized by the parameter K_F (see Table 4-2), has been lowered after the first regeneration for all resins at all resin doses except IRA900 and IRA958 undergoing two regenerations. This may indicate regeneration might not have been completed. Nevertheless, the regeneration efficiencies for IRA900 and IRA958 calculated in Table A-7 in Appendix A were remarkably high, indicating almost complete recovery of colour removal ability after regeneration. This suggests that an exchange capacity characterized by a high enough K_F is sufficient for excellent removal of colour from the sample tested. Even though the resin capacity of IRA458 decreased after the first regeneration (see Table 4-2), the regeneration recovered approximately 94% of removal efficiency (Table A-7 in Appendix A).

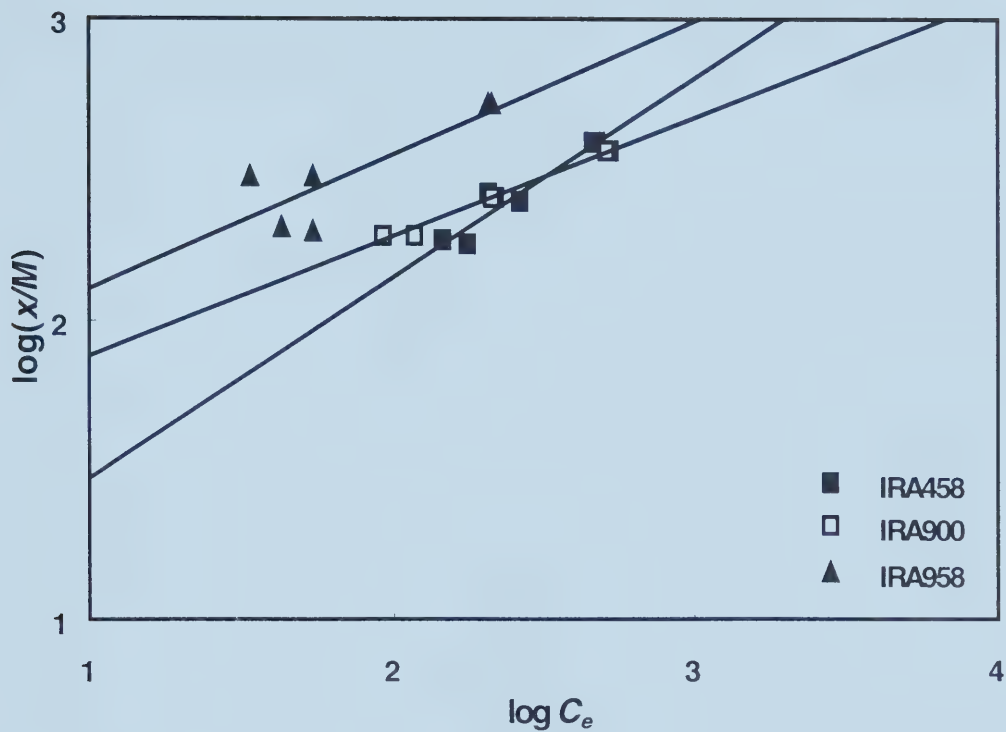


Figure 4-9 Linearised Freundlich isotherms for resins after the first regeneration in colour removal (25°C, Final effluent C_0 : 1240 TCU, Shaker : 250 RPM, Resin dose : 2, 4, 6 g/L).

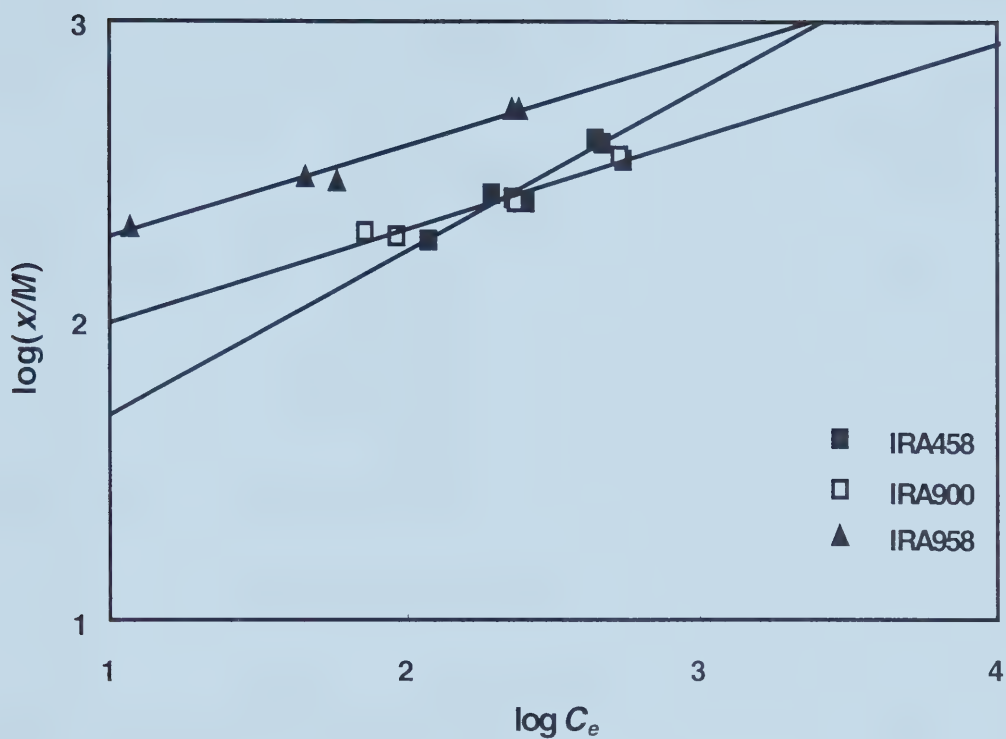


Figure 4-10 Linearised Freundlich isotherms for resins after the second regeneration in colour removal (25°C, Final effluent C_0 : 1240 TCU, Shaker : 250 RPM, Resin dose : 2, 4, 6 g/L).

Table 4-2 The Freundlich parameters for three effective resins on colour removal (20°C, Final effluent C_0 : 1240 TCU, Contact time : 2 days, Shaker : 250 RPM, Regenerant : 1 N NaOH in combination with 1 N NaCl).

	Resin	K_F (TCU-L/g)	n	Coefficient of Determination (r^2)
1 st ion exchange	Amberlite IRA458	16.76	1.881	0.96
	Amberlite IRA900	38.34	2.837	0.97
	Amberlite IRA958	67.20	3.114	0.98
2 nd ion exchange	Amberlite IRA458	6.368	1.498	0.93
	Amberlite IRA900	30.13	2.520	0.98
	Amberlite IRA958	44.44	2.220	0.72
3 rd ion exchange	Amberlite IRA458	13.80	1.837	0.96
	Amberlite IRA900	48.17	3.209	0.97
	Amberlite IRA958	93.54	3.300	0.98

4.2 Colour Removal Column Testing

4.2.1 Breakthrough Studies

The batch studies showed that IRA458, IRA900, and IRA958 are effective to remove colour from the pulp mill final effluent. The following column breakthrough testing has been conducted to verify the results determined from the batch studies. In addition to the verification, the column testing could indicate optimum operating parameters and resin behaviour over time during runs for colour removal (breakthrough curves). Breakthrough point could indicate a proper point to initiate regenerating columns to prevent column effluent from seriously deteriorating.

Figure 4-11 contains the results of column breakthrough testing expressed as fractional colour remaining (residual colour divided by initial colour) versus the number of bed volumes (BV) of sample put through the column. Even though the raw water was filtered prior to being input to columns, clogging occurred in the column containing IRA458. While running the column, the top of resin bed was observed to subside. At the same time, the flowrate uncontrollably dropped regardless of opening the valve at the outlet. The clogging problem might be attributed to the reduction of available flow paths due to settlement of IRA458 or to the presence of air bubbles that had not been removed during the packing of resins. IRA458, unlike IRA900, is transparent which makes it hard to differentiate air bubbles from resins. The experimental error for packing might be overlooked.

IRA458 is a gel type resin which tends to form aggregates of beads while IRA900 remains discrete. This aggregation might cause blockage of pores between resin beads and prevent the resins from evenly contacting effluent.

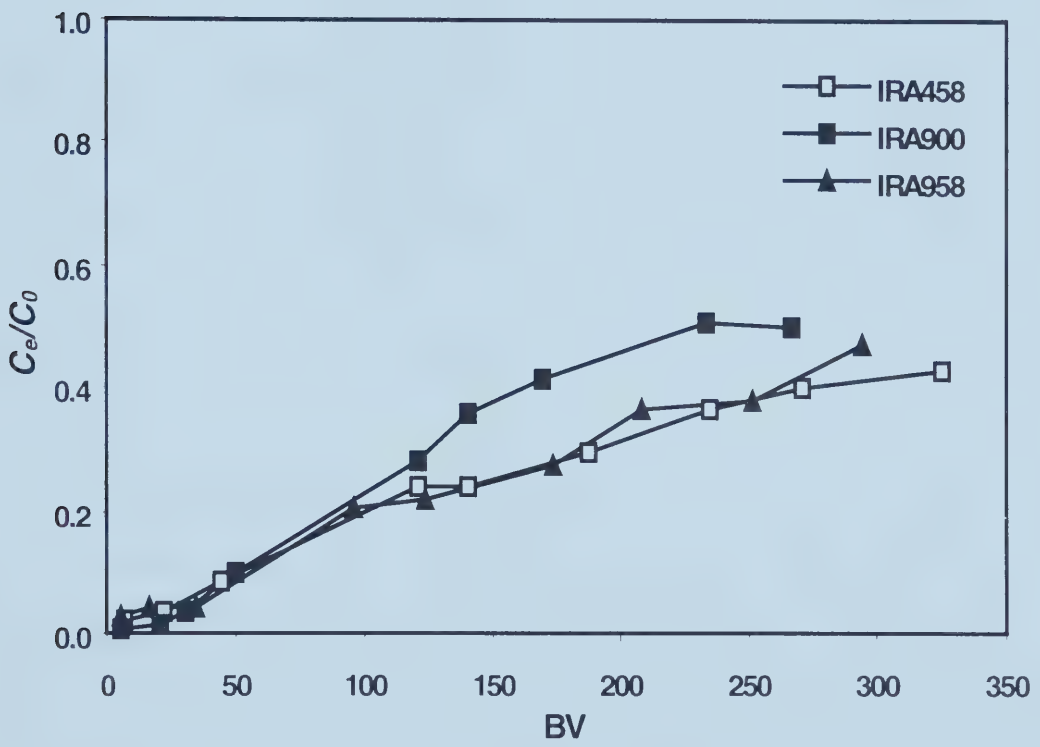


Figure 4-11 Breakthrough curves for selected resins during colour removal, expressed as fractional colour remaining (C_e/C_0) versus the number of bed volumes (BV) put through the column (18°C, Final effluent C_0 : 1240 TCU, 1 BV : 57 mL, EBCT : 12 mins).

The observed reduction of bed depth during the operation of the column could be explained by the aggregation of the IRA458 resin beads. This might increase the potential for the column to clog.

Preliminary column tests were conducted to optimise resin bed depth and bed contact time for subsequent column testing. The testing results established the resin bed depth of 20 centimetres and the bed contact time of 12 minutes. The results are given in Appendix B. While conducting these breakthrough studies, no sharp increase in effluent colour was observed. A point to regenerate columns could be selected referring to the studies up to colour discharge requirement.

The results indicated that the dynamic behaviour of the three resins was very similar from one resin to another. IRA458, a gel type resin, unlike IRA900 or IRA958, which is macroporous, seemed to be closely packed in the column through visual observation and approximate measurement of the used resin weight after the ion exchange. Of the three resins, IRA458 treated the greatest amount of the sample prior to approximately 50% colour breakthrough.

4.2.2 Elution Studies

The objective of the elution studies was to verify whether 1 *N* NaOH in combination with 1 *N* NaCl is also an effective regenerant in continuous flow mode, and to determine the effect of reagent flowrate on regeneration. This elution study could

also show how much regenerant is needed to regenerate columns. During the elution studies, the colour released by the resins as they were regenerated was measured over time. The resins used in this study had previously been used in columns to remove colour from final effluent. Colour removal using continuous-flow ion-exchange columns was carried out until the colour concentration in the column effluent (C_e) reached 0.3 of the influent colour concentration (C_0). The columns were then taken out of service, rinsed thoroughly with deionised water, and regenerated. Figures 4-12 and 4-13 are the plots of the results of the elution of colour from ion exchange columns as a function of bed volumes of regenerant used at flowrates of 3.6 and 4.5 mL/min, respectively.

The results shown in Figures 4-12 and 4-13 indicate that 1 *N* NaOH in combination with 1 *N* NaCl released colour from the IRA 958 resin very efficiently in the continuous-flow mode, confirming the earlier batch test results. A comparison of Figure 4-12 to 4-13 shows that approximately the same volume of regenerant was required at each flow rate. These results indicate that the amount of regenerant required is relatively insensitive to the superficial velocity at which it is applied (within the range tested). For the size of column used in this study (1.9×10^{-2} m inner diameter), application of regenerant at a rate of 3.6 mL/min results in a superficial velocity of 12.7 mm/min. Increasing this velocity by approximately 25% to 15.9 mm/min (4.5 mL/min) had a negligible effect on the rate of colour elution from the resin bed. More elution studies with higher flowrates must be investigated since

higher flowrates could save space for the ion-exchange set-up system or column capacity.

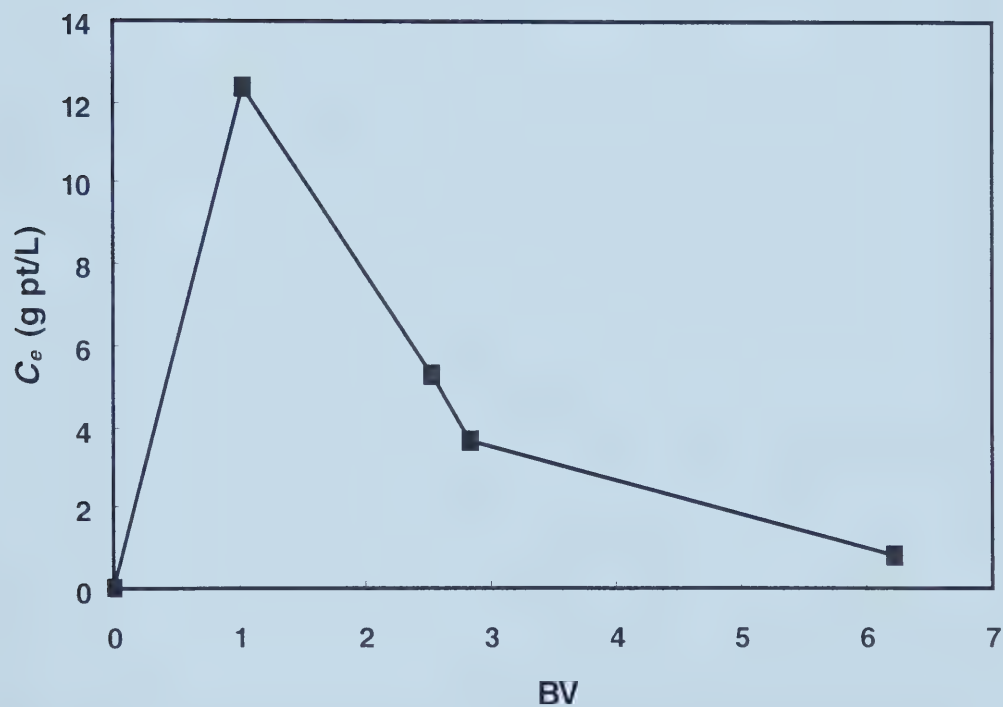


Figure 4-12 Colour elution curves during regeneration of IRA958 using the combination of 1N NaCl and 1N NaOH at 3.6 mL/min flowrate (18°C, 1 BV : 57 mL, EBCT : 16 mins)

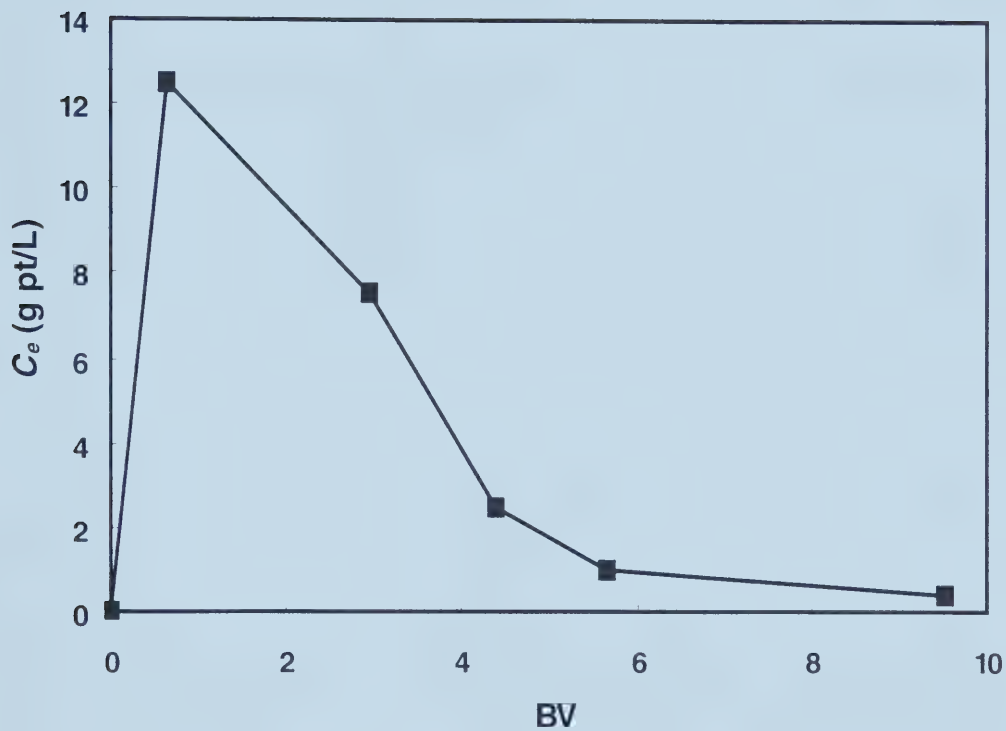


Figure 4-13 Colour elution curves during regeneration of exhausted IRA958 with the combination of 1 *N* NaCl and 1 *N* NaOH at 4.5 mL/min flowrate (18°C, 1 BV : 57 mL, EBCT : 13 mins)

4.2.3 Summary of Colour Removal Results

Based on all of the results of resin dose study with various effluents, the best resins for colour removal were IRA900 and IRA958. IRA458 also showed good colour removal ability during regeneration studies. While these resins were able to achieve good colour removal, they also released considerable amounts of chloride ion into solution during the exchange process. The chloride ions must therefore be removed in subsequent treatment if the treated wastewater is to be re-used in the pulping process.

The performance of WBA resins in the treatment of D and E_{op} stage effluents is of interest. Two WBA resins, IRA67 and IRA92, removed colour well from the D stage effluent and from the final effluent. However, they were not able to achieve good colour removal from the alkaline E_{op} stage effluent. This is because the WBA resins function best under acidic to neutral pH condition as mentioned in Section 2.4.3. Exchange with all of three types of effluents revealed that IRA900 and IRA958, which are both macroporous resins, were very effective to remove colour. IRA900 readily broke down by the stirring bars. This apparently improved its ability to remove colour. This may have been because this breakage allowed the colour causing compounds to interact with more of the resin exchange sites, which implies that the extent of colour removal may have been limited by access to exchange sites within intact resin beads due to the relative sizes of the resin pores and colour causing molecules. Therefore, larger pore size resins would be beneficial to decolourisation.

NaOH alone was not able to release colour-causing compounds captured on exchange sites of resins by exchange with hydroxide ions. However, 1 *N* NaOH in combination with 1 *N* NaCl achieved remarkably efficient regeneration.

4.3 Chloride Removal

4.3.1 Chloride Removal by Selected Resins

The study of resin dose effect on chloride removal was conducted to determine effective resins to remove chloride from pulp mill effluents. Figure 4-14 demonstrates the result of chloride removal batch tests using four resins including IRA67 and IRA92 in the free base form, and IRN78 and 4400OH in the hydroxide form. Raw lagoon influent sample was used for this study. Regardless of the resin dose applied, only the hydroxide form resins, IRN78 and 4400OH removed chloride. IRN78 and 4400OH at 10 g/L achieved removal of approximately 50% and 70%, respectively. These two resins showed that they have a potential to reduce chloride concentration in pulp mill effluents.

4.3.2 Regeneration Studies

Regeneration studies were conducted in the batch mode to determine effective reagents to regenerate exhausted resins after chloride removal. Raw final effluent was tested in this batch experiment. Figures 4-15 and 4-16 illustrate the results of testing NaOH as a regenerant.

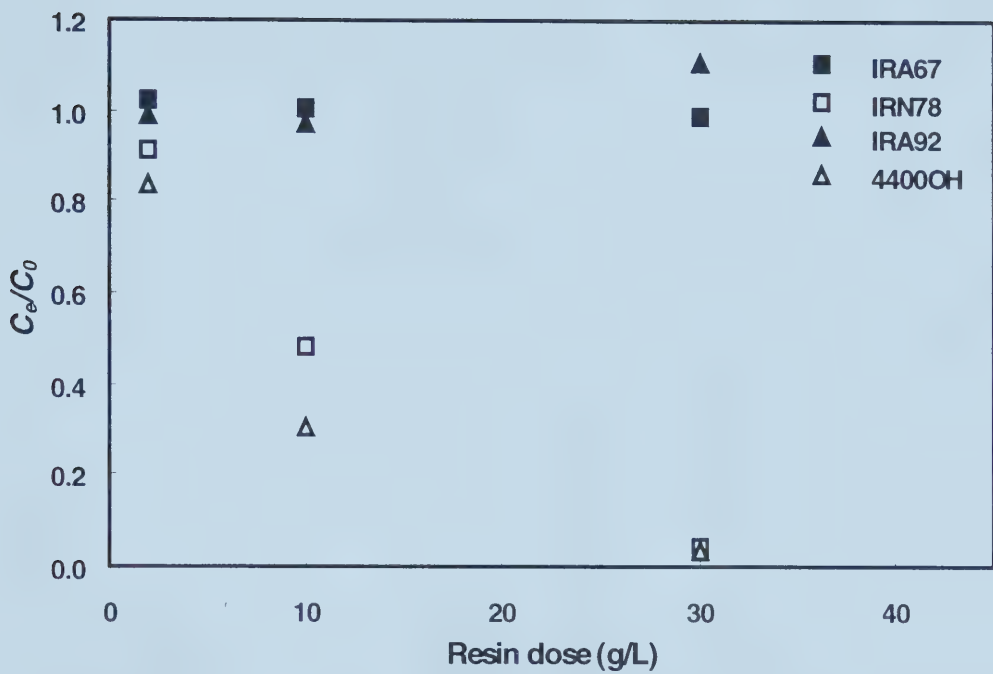


Figure 4-14 Chloride removal from lagoon influent using four anionic resins (21°C, C_0 : 240 ppm, Contact time : 1 day)

Figure 4-15 is a plot of the data obtained from the regeneration study based on chloride removal from final effluent. Six anionic resins were tested over four chloride removal cycles and three regeneration cycles using 1 N NaOH. Of the resins tested, IRN78 and 4400OH performed much better than the others during the

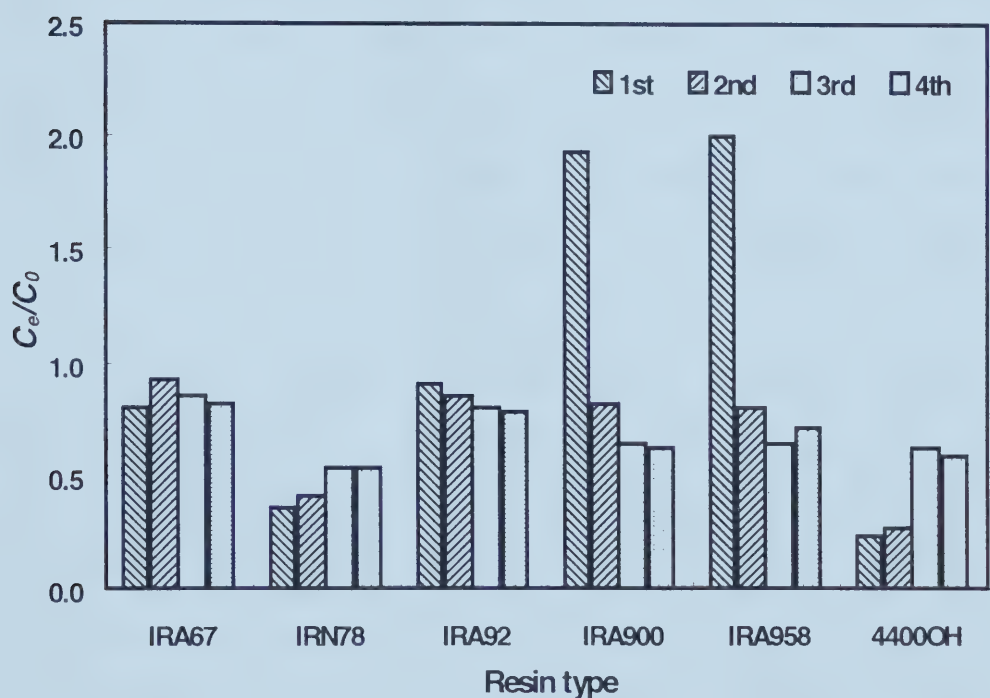


Figure 4-15 Regeneration of six anionic exchangers removing chloride from final effluent using 1 N NaOH (21°C, C_0 : 240 ppm, Resin dose : 10 g/L, Contact time : 1 day).

first two ion exchange cycles even though the chloride removal efficiency deteriorated with repeated regeneration. The chloride concentration in the samples actually increased when virgin IRA900 and IRA958 were used because of the exchange of Cl^- from the resin with colour causing compounds in the samples, as shown in Figure 4-15. After the regeneration with 1 *N* NaOH, the IRA900 and IRA958 can be assumed to possess hydroxide ions at many of the exchange sites. Therefore, after regeneration these resins accomplished removal of chloride comparable to the WBA resins, IRA67 and IRA92 (see Figure 4-15). Figure 4-16 is a plot of the data obtained from the regeneration study using blended bleach wastewater and six anionic resins for chloride removal and regeneration cycles using 1 *N* NaOH.

A comparison of Figure 4-16 to Figure 4-15 shows that IRN78 and 4400OH seemed to remove chloride more readily from the combined sample than from the final effluent. The chloride removal efficiency achieved by IRN78 and 4400OH regenerated with 1 *N* NaOH reached more than 70% chloride removal (see Figure 4-16). More concentrated NaOH solutions (2 *N* and 3 *N*) were studied as regenerants, but these could not improve the regeneration efficiency. The higher densities of these solutions caused the resins to float on the reagent liquid surface so that resins could make a proper contact with these higher normality regenerants. These results are given in Table A-9 in Appendix A.

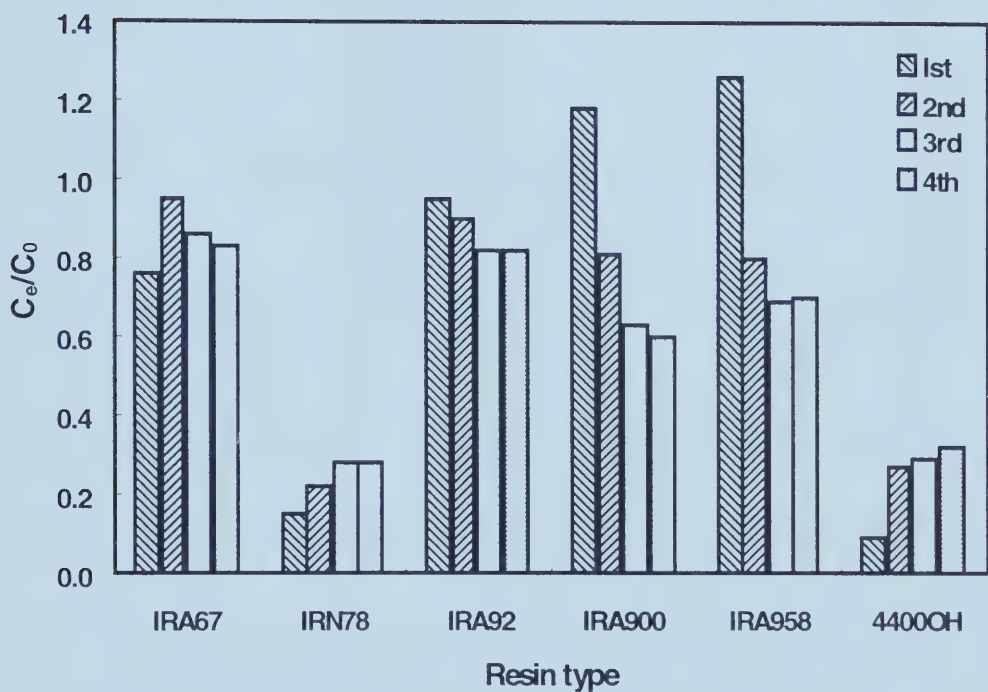


Figure 4-16 Regeneration of six anionic resins removing chloride from blended bleach wastewater using 1 *N* NaOH (21°C, C_0 : 190 ppm, Resin dose : 10 g/L, Contact time : 1 day).

4.3.3 Chloride Isotherm Testing

Isotherm tests were conducted in duplicate at the resin doses of 4, 10, and 25 g/L. The objective of the isotherm testing using IRN78 and 4400OH was to determine their relative exchange capacities during chloride removal from raw final effluent. Raw data expressed as residual chloride concentration divided by initial chloride of chloride isotherm testing are given in Table A-10. Table 4-3 lists the Freundlich parameters from the isotherm tests using virgin and regenerated IRN78 and 4400OH. Based on the K_F values from tests, virgin 4400OH was found to have higher exchange capacity than virgin IRN78. On the other hand, the K_F values of regenerated IRN78 resins were slightly higher than regenerated 4400OH, but the coefficients of determination (r^2) associated with this model calibration were rather low, indicating that the linearised Freundlich model did not represent the data adequately.

The Langmuir model was also applied to determine whether it could provide a better fit to the data from the chloride isotherm studies. The resulting model parameter values and coefficients of determination (r^2) are given in Table 4-4. The fit of the Langmuir model to the data from tests using 4400OH for both the second and the third ion exchange (see Table 4-4) was better than that of the Freundlich model (see Table 4-3). However, the r^2 values associated with the Langmuir model fit (see Table 4-4) for the data from the IRN78 isotherm tests were still very low. This suggests that the resins (particularly IRN78) were not evenly regenerated.

Table 4-3 The Freundlich parameters for two effective resins on chloride removal (20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 N NaOH, Resin dose : 4, 10, and 25 g/L)

	Resin	K_F (ppm-L/g)	n	Coefficient of Determination (r^2)
1 st ion exchange	Amberlite IRN78	3.76	3.31	0.9
	Amberjet 4400OH	5.09	4.26	0.83
2 nd ion exchange	Amberlite IRN78	5.33	8.21	0.28
	Amberjet 4400OH	1.17	2.64	0.56
3 rd ion exchange	Amberlite IRN78	2.19	3.66	0.31
	Amberjet 4400OH	0.30	1.71	0.91

A possible cause for this may have been poor contact between the resin and the regenerant. It was observed that some of both IRN78 and 4400OH stuck to the flask wall during the test. To transfer the sticky beads, a spatula was used to draw them out. During ion exchanges, some resins sticking to the flasks might not sufficiently contact samples. The possible reason for quite low r^2 of model fits to data from the second or third ion-exchange might be attributed to some bead loss during transfer of resins from flasks to flasks. Nevertheless, based on the prior regeneration studies, it can be stated that IRN78 and 4400OH were able to remove more chloride per unit mass of resin than the other resins tested. The parameter of $(x/M)_{max}$ is related to resin capacity. This might show performance of resins. The parameters from ion

exchanges using the two virgin resins indicate that IRN78 is a little better than 4400OH in the maximum surface concentration at resins. This Langmuir equation unlike Freundlich isotherm requires homogeneous nature of resins. Empirical Freundlich parameters are believed to give data better representation. Chloride isotherm tests could not show which resin of the two is better to remove chloride.

Table 4-4 Langmuir parameters for IRN78 and 4400OH on chloride removal (20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 N NaOH)

	Resin	$(x/M)_{max}$	b	Coefficient of Determination (r^2)
1 st ion exchange	Amberlite IRN78	20	0.040	0.89
	Amberjet 4400OH	18	0.066	0.82
2 nd ion exchange	Amberlite IRN78	11	0.081	0.22
	Amberjet 4400OH	14	0.008	0.69
3 rd ion exchange	Amberlite IRN78	11	0.024	0.26
	Amberjet 4400OH	16	0.003	0.95

4.4 Chloride Removal Column Testing

The column for chloride removal was designed to follow that for colour removal since substantial increases in chloride concentration were observed during decolourisation.

4.4.1 Breakthrough Study

Based on the effective resin study and regeneration study for chloride removal, breakthrough study was investigated to verify chloride removal with the best effective resins tested, IRN78 and 4400OH in a continuous flow and examine the resin behaviour with run time.

Figure 4-17 is a plot of data of breakthrough studies using IRN78 and 4400OH in operating design parameters shown in Table 4-5. Sharp increase in chloride concentration at the output of the column containing each resin initiated after 25 BVs of final effluent put through (see Figure 4-17).

Table 4-5 Design parameters operated in columns with each IRN78 and 4400OH

	IRN78	4400OH
BV (mL)	26.1	25.5
EBCT (min)	6.3	7.0
Flowrate (mL/min)	4.1	3.6

For the determination of breakthrough point, it is needed to frequently measure the output chloride concentration between 20 and 40 in BV. The difference

(see Figure 4-17) of the steepness while developing breakthrough curves using IRN78 and 4400OH were possibly made by the variation of parameters given in Table 4-5.

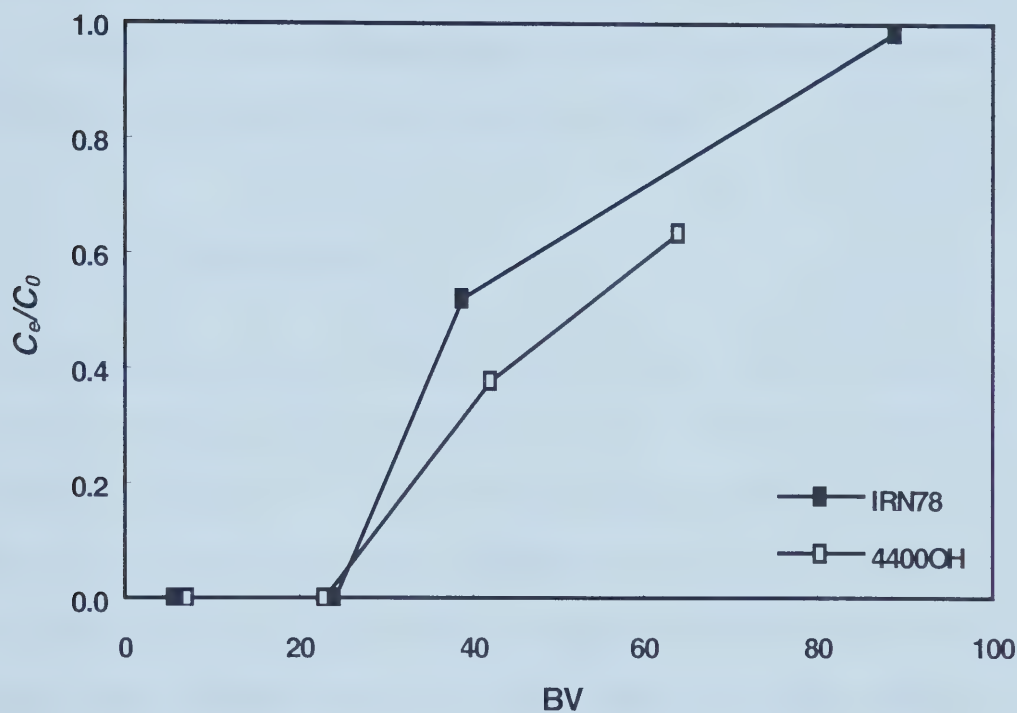


Figure 4-17 Chloride breakthrough curves with IRN78 and 4400OH at 18°C (Initial input water C_0 : 510 ppm)

The breakthrough test of a little deeper bed and lower flowrate in a column with IRN78 than that containing 4400OH might produce the more favourable curve, which is in proportional to steepness of the curve after the breakthrough point (see Figure 4-17). These sharp increases in released chloride concentration (see Figure 4-17) occurring after the breakthrough points are useful for designing optimum operating parameters, especially a point to regenerate columns.

4.4.2 Elution Study

The elution study was aimed at verifying the results obtained from batch testing that IRN78 is an effective resin for chloride removal and that 1 *N* NaOH is an effective regenerant. The results of the chloride elution study using IRN78 are shown in Figure 4-18. The design parameters for the elution study are given in Table 4-6. Final effluent was fed into a colour removal column containing IRA958 and then the column effluent, retaining little or no colour but having a high concentration of chloride, was pumped into the chloride removal column. The influent to the chloride removal column contained 510 ppm of chloride due to the chloride initially contained in the sample of final effluent (290 ppm) and the release of chloride into the sample during decolourisation with IRA958. The column containing IRN78 was run until the chloride concentration in the column effluent (C_e) reached 0.3 of the influent chloride concentration (C_0). The column was then taken out of service, rinsed thoroughly with deionised water and regenerated with 1 *N* NaOH. The results of the elution study are shown in Figure 4-18. These results indicate relatively slow and incomplete release

of chloride from the resin during regeneration, even at the low superficial flowrate of 7.0 mm/min chosen for this elution study. More concentrated NaOH might improve the chloride release in columns. The use of deeper resin beds should also be investigated.

Table 4-6 Operating parameters for chloride removal and then elution (18°C, 1 BV : 28 mL).

	Chloride removal tests	Chloride elution tests
Cl ⁻ in influent, C ₀ (ppm)	510	0
Flowrate (mL/min)	4	2
EBCT (min)	7	14
Throughput (BV)	189*	17**

* final effluent sample
** regenerant (1 N NaOH)

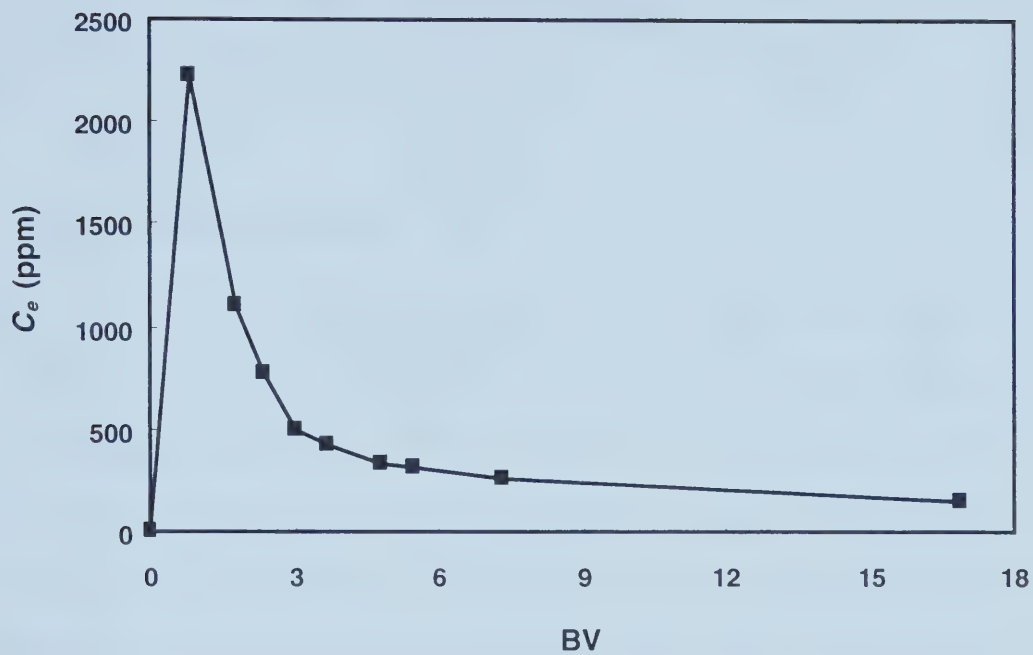


Figure 4-18 Chloride elution curve during regeneration of exhausted IRN78 with 1 *N* NaOH

5 Conclusions

5.1 Colour removal

Out of all of the ion exchange resins tested through resin doses, regeneration, and isotherm studies, IRA958 proved to be the best resin for colour removal from lagoon influent and E_{op} stage effluent. IRA900 and IRA67 were best to remove colour of D stage effluent. IRA458 also showed a good ability to remove colour from final effluent and was well regenerated. The key concern for ion exchange is how well exhausted resins can be regenerated and reused in the system. 1 *N* NaOH in combination with 1 *N* NaCl tested as a regenerant was remarkably capable of regenerating IRA458, IRA900, and IRA958 having completely captured colour-causing compounds.

IRA67 and IRA92 can be also promisingly used for decolourisation with an advantage of no chloride addition proven in resin dose effect study on chloride removal. IRA67 and IRA92 are in the form of free base, which means no base (anion) on the exchange site. IRA67 removed a large amount of colour from lagoon influent during batch tests with 10 g IRA67/L and almost all of the colour of D stage effluent at 30 g IRA67/L. IRA92 removed colour very well from both lagoon influent and D stage effluent at 30 g IRA92/L. These resins showed remarkable

colour removal efficiency and sufficient application feasibility to remove colour causing compounds in a proper range of pH (0 – 7).

IRA67 and IRA92 can be also promisingly used for decolourisation with an advantage of no chloride addition proven in resin dose effect study on chloride removal. IRA67 and IRA92 are in the form of free base, which means no base (anion) on the exchange site. IRA67 removed considerable amounts of colour from lagoon influent during batch tests with 10 g IRA67/L and almost all of the colour of D stage effluent at 30 g IRA67/L. IRA92 achieved excellent colour removal from both lagoon influent and D stage effluent at 30 g IRA92/L. These resins showed remarkable colour removal efficiency and sufficient application feasibility to remove colour causing compounds in a proper range of pH (0 – 7).

5.2 Chloride removal

Resin dose and regeneration studies on chloride removal in the batch mode showed IRN78 and 4400OH were the best among the resins tested, but had a modest chloride removal of approximately 65%. As expected, chloride ions were not removed very readily. In spite of this result, it implies that ions with ion exchange affinities to anionic resin that are greater than that of chloride could be removed to greater degrees than chloride. This might account for the relatively low chloride removal due to a lack of available exchange sites since most of exchange sites might be occupied by these other anions.

5.3 Optimal point of combined colour and chloride removal within a kraft pulp mill

One of goals of this study was to determine the optimal point of ion exchange application within a pulp mill. The results of this investigation indicate that the process could be applied either to a blended bleach plant waste stream, just upstream of the lagoon inlet, or at its outlet using either IRA459, IRA900, or IRA958. For the determination of optimal point for the chloride removal column, further chloride removal study is required. However, based on the results of the colour removal studies, the best point to apply the chloride removal may well be following the colour removal columns.

5.4 Combined colour and chloride removal

Even though the three best resins (IRA458, IRA900, and IRA958) for decolourisation have a potential for complete colour removal, they release chloride ions, replaced by colour-causing compounds. To avoid the addition of chloride to the wastewaters during decolourisation, IRN78 or 4400OH could be used for colour and chloride removal at the same time since the two resins showed a modest colour and chloride removal efficiency.

IRN78 showed modest colour removal ability although it was not as great as that achieved by IRA458, IRA900, and IRA958. Batch tests using IRN78 at 30 g/L achieved approximately 70% colour removal from D stage effluent and around 50%

from lagoon influent and E_{op} stage effluent. This removal could undoubtedly be improved by using a higher resin dose. In order to improve the removal efficiency, a series of columns or one deep bed column packed with IRN78 or 4400OH can be employed.

6 Recommendations

The following recommendations are suggested to improve chloride removal:

- to determine more effective resins than IRN78 or 4400OH;
- to test a series of columns for chloride removal; and
- to treat the effluents with deeper bed columns.

The high feasibility of application of the ion exchange technology to the pulp mill systems was sufficiently shown by determining effective resin and regenerant for decolourisation. Further pilot scale study is recommended to establish ion exchange advantages and disadvantages for treatment of pulp mill effluents and what optimum operating parameters are for a full scale plant. In the meantime, the pilot scale study is needed to fully prove how well the ion exchange contributes to the development of progressive system closure.

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8 Appendices

8.1 Appendix A

Table A-1 Sample pH after decolourisation of lagoon influent (initial pH 7.5-7.8)

(Data used to prepare Figure 4-1).

	Resin dose (g/L)			
	0	2	10	30
IRA67	7.8	8.3	8.7	9.0
IRN78	7.8	8.8	11.3	11.6
IRA92	7.8	7.8	7.8	8.2
IRA400	7.8	8.0	9.7	11.3
IRA402	7.5	7.6	7.7	7.7
IRA900	7.5	8.0	7.3	7.4
IRA958	7.5	7.8	7.3	7.2
4400OH	7.8	8.8	11.1	11.5

Table A-2 Sample pH after decolourisation from D stage effluent (initial pH 2.2-2.3)
(Data used to prepare Figure 4-2).

	Resin dose (g/L)			
	0	2	10	30
IRA67	2.2	2.3	4.2	7.4
IRN78	2.2	2.4	3.8	11.1
IRA92	2.2	2.4	4.1	6.1
IRA400	2.2	2.2	2.5	4.0
IRA402	2.3	2.3	2.3	2.5
IRA900	2.3	2.3	2.2	2.2
IRA958	2.3	2.2	2.2	2.2
4400OH	2.2	2.2	3.4	11.2

Table A-3 Sample pH after decolourisation from E_{op} stage effluent (initial pH 11.4)
(Data used to prepare Figure 4-3).

	Resin dose (g/L)			
	0	2	10	30
IRA67	11.4	11.3	11.3	11.3
IRN78	11.4	11.4	11.8	12.1
IRA92	11.4	11.3	11.4	11.3
IRA400	11.4	11.5	11.7	11.9
IRA402	11.4	11.4	11.4	11.3
IRA900	11.4	11.4	11.4	11.4
IRA958	11.4	11.4	11.2	10.5
4400OH	11.4	11.5	11.9	12.1

Table A-4 Regeneration studies with reagents in diverse ratios of NaOH to NaCl expressed as C_e/C_0 (Final effluent colour concentration C_0 : 910 - 1220 TCU, 21°C, Resin dose : 10 g/L, Contact time : 1 day).

NaOH (N)	NaCl (N)	Resin type	1 st	2 nd	3 rd
1	0.01	IRA458	0.22	0.76	0.88
		IRA900	0.17	0.45	0.71
		IRA958	0.11	0.70	0.90
1	0.1	IRA458	0.22	0.71	0.81
		IRA900	0.04	0.32	0.35
		IRA958	0.24	0.54	0.70
1	1	IRA458	0.23	0.27	0.20
		IRA900	0.10	0.05	0.06
		IRA958	0.08	0.05	0.01
1.7	0.5	IRA458	0.25	0.21	0.21
		IRA900	0.11	0.09	0.10
		IRA958	0.09	0.19	0.03

Table A-5 Regeneration studies with reagents in diverse ratios of NaOH to NaCl expressed as C_e/C_0 . (Lagoon influent colour concentration C_0 : 860 TCU, 21°C, Resin dose : 30 g/L, Contact time : 1 day).

	0.475 N NaOH + 0.085 N NaCl		0.495 N NaOH + 0.017 N NaCl	
C_e/C_0	1 st	2 nd	1 st	2 nd
IRA67	0.06	0.99	0.09	0.96
IRN78	0.47	0.60	0.48	0.72
IRA92	0.07	0.19	0.08	0.65
IRA900	0.01	0.02	0.03	0.19
IRA958	0.02	0.00	0.02	0.17
4400OH	0.63	0.85	0.65	0.93

Table A-6 Colour isotherm data expressed as C_e/C_0 (Final effluent C_0 : 1240 TCU, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 N NaOH in combination with 1 N NaCl) (Data used to prepare Figures 4-8 through 4-10).

C_e/C_0	Resin dose (g/L)	IRA458	IRA900	IRA958
1 st	2	0.33	0.43	0.28
	4	0.15	0.19	0.08
	6	0.08	0.07	0.02
2 nd	2	0.38	0.43	0.17
	4	0.19	0.18	0.04
	6	0.13	0.09	0.04
3 rd	2	0.37	0.44	0.19
	4	0.18	0.19	0.04
	6	0.10	0.07	0.00

Table A-7 Colour isotherm data expressed as regeneration efficiency (% of colour removal achieved after regeneration relative to that achieved by virgin resin) (Final effluent C_0 : 1240 TCU, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 N NaOH in combination with 1 N NaCl) (Data used to prepare Figures 4-8 through 4-10).

Regeneration	Resin dose (g/L)	IRA458	IRA900	IRA958
1 st	2	93	101	115
	4	95	102	105
	6	95	99	98
2 nd	2	95	98	112
	4	96	101	104
	6	98	101	102

Table A-8 Regeneration using 0.5 N NaOH expressed as C_e/C_0 (Final effluent C_0 : 230 ppm, 21°C, Resin dose : 10 g/L, Contact time : 1 day)

C_e/C_0	1 st	2 nd	3 rd
IRA67	1.01	1.02	0.97
IRN78	0.59	0.77	0.72
IRA92	1.15	0.94	0.93
IRA900	2.29	0.80	0.84
IRA958	2.29	0.75	0.87
4400OH	0.59	0.82	0.81

Table A-9 Regeneration using 1, 2, and 3 N NaOH expressed as C_e/C_0 (18°C, Final effluent C_0 : 290 ppm, Resin dose : 10g/L, contact time : 1 day, Regenerant conc. : 1, 2, & 3 N NaOH, shaker : 250 RPM).

NaOH (N)		1 st	2 nd	3 rd
1	IRN78	0.42	0.47	0.61
	4400OH	0.27	0.30	0.73
2	IRN78	0.61	0.84	0.90
	4400OH	0.66	0.92	0.97
3	IRN78	0.59	0.88	0.89
	4400OH	0.65	1.03	1.00

Table A-10 Chloride isotherm tests expressed as C_e/C_0 (Final effluent C_0 : 290 ppm, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 N NaOH) (Data used to prepare Tables 4-3 and 4-4).

Resin dose (g/L)	1 st		2 nd		3 rd	
	IRN78	4400OH	IRN78	4400OH	IRN78	4400OH
4	0.71	0.72	0.83	0.87	0.83	0.89
10	0.48	0.50	0.69	0.65	0.73	0.74
25	0.09	0.07	0.22	0.41	0.32	0.52

Table A-11 Chloride isotherm tests expressed as regeneration efficiency in % (Final effluent C_0 : 290 ppm, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 N NaOH) (Data used to prepare Tables 4-3 and 4-4).

Resin dose (g/L)	1 st		2 nd	
	IRN78	4400OH	IRN78	4400OH
4	57	44	57	36
10	58	70	51	52
25	86	63	74	51

8.2 Appendix B

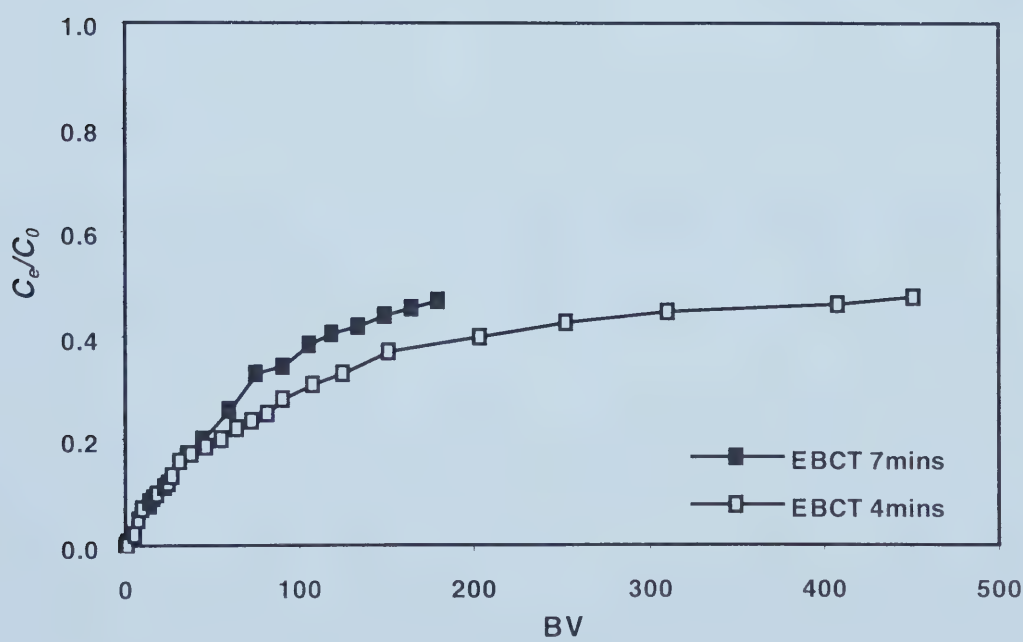


Figure B-1 Breakthrough study on colour removal using IRA900 at 4 and 7 minutes of EBCT (Final effluent C_0 : 1240 TCU, Resin bed depth : 10 cm, 1 BV : 28 mL)

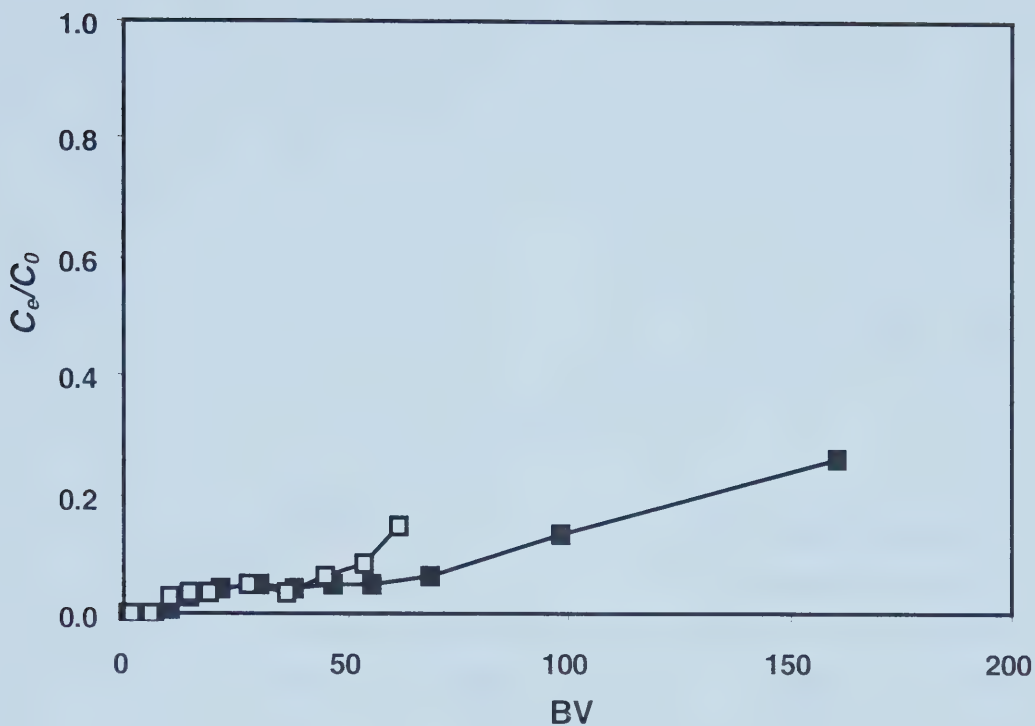


Figure B-2 Breakthrough study on colour removal using IRA900 at 14 minutes of EBCT in duplicate (Final effluent C_0 : 920 TCU, Resin bed depth : 23 cm, 1 BV : 64 mL).

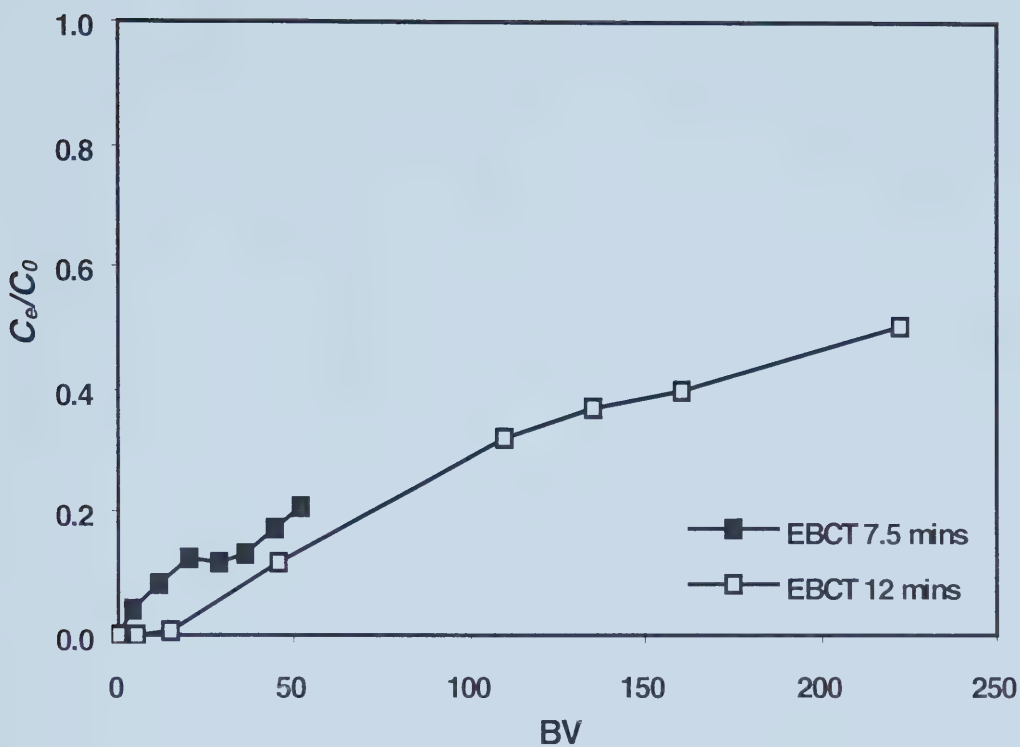


Figure B-3 Breakthrough study on colour removal with IRA900 at 7.5 and 12 minutes of EBCT (Final effluent C_0 : 1190 - 1330 TCU, Resin bed depth : 20 cm, 1BV : 57 mL)

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